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[54] **PROCESS AND APPARATUS FOR CONTROLLING REACTION TEMPERATURES**

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[51] **Int. Cl.**[6] **F28D 7/00**; B01J 8/02; F28F 27/02; F01P 7/10

[52] **U.S. Cl.** **422/200**; 422/198; 422/211; 165/96; 165/97; 165/98; 165/102; 165/170

[58] **Field of Search** 422/198, 206, 422/200, 138, 211, 213, 238, 236, 222; 165/96, 97, 101, 102, 113, 170, 98

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Assistant Examiner—Christopher Y. Kim
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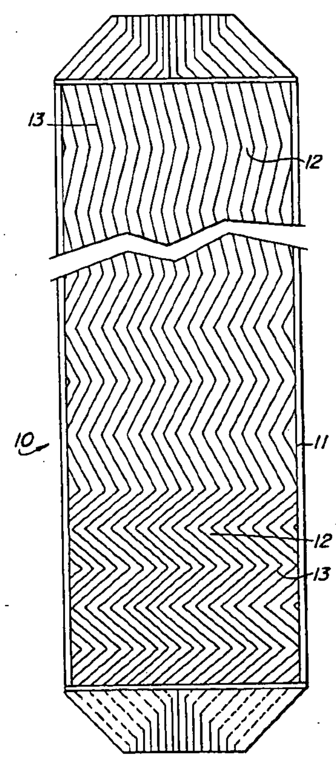
[57] **ABSTRACT**

A reactor arrangement and process for indirectly contacting a reactant stream with a heat exchange stream uses an arrangement of corrugated heat exchange plates to control temperature conditions by varying the number and/or the arrangement of the corrugations along the plates. The reactor arrangement and process of this invention may be used to operate a reactor under isothermal or other controlled temperature conditions. The variation in corrugation arrangements within a single heat exchange section is highly useful in maintaining a desired temperature profile in an arrangement having a cross-flow of heat exchange medium relative to reactants. The corrugations arrangement eliminates or minimizes the typical step-wise approach to isothermal conditions.

19 Claims, 13 Drawing Sheets



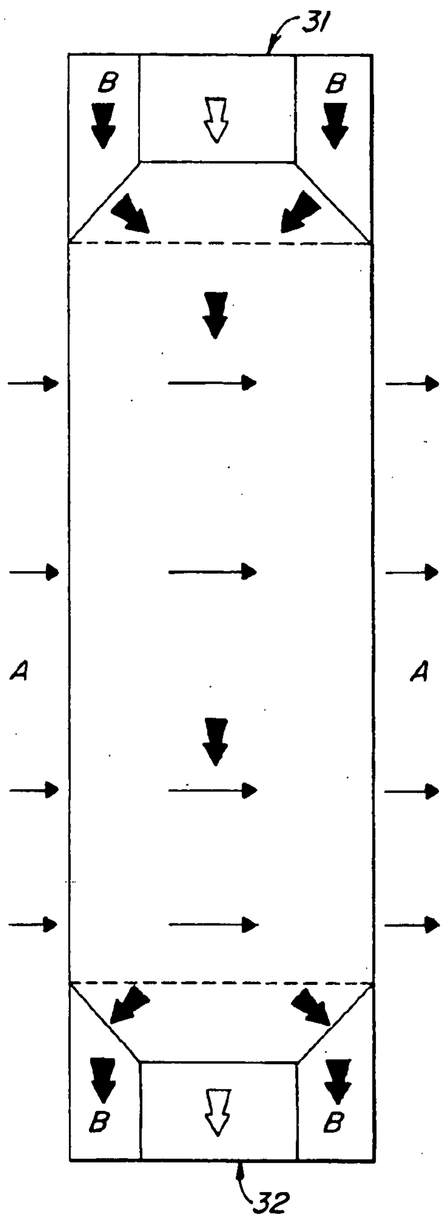


Fig. 1

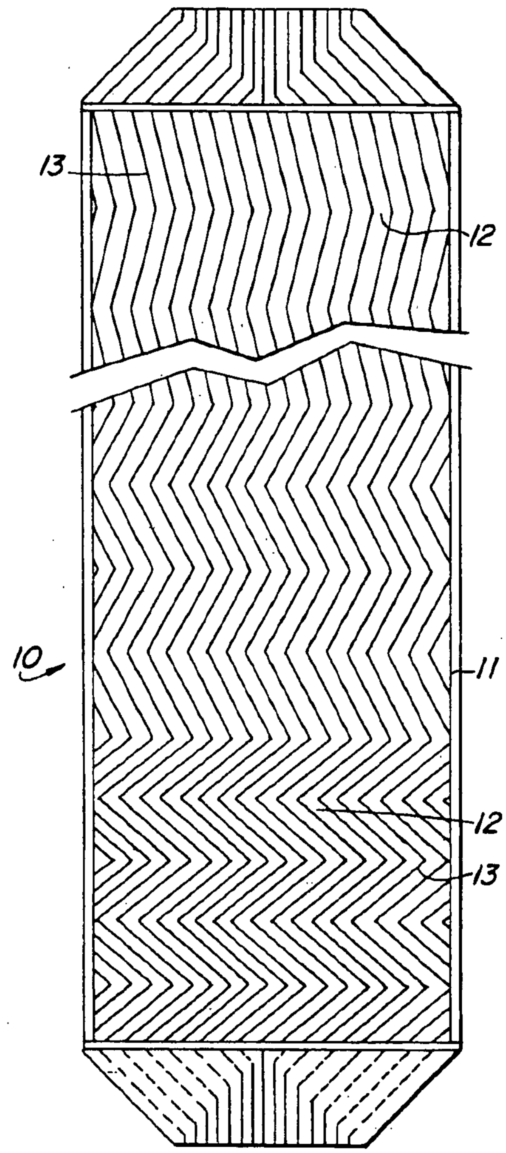


Fig. 2

Fig. 3

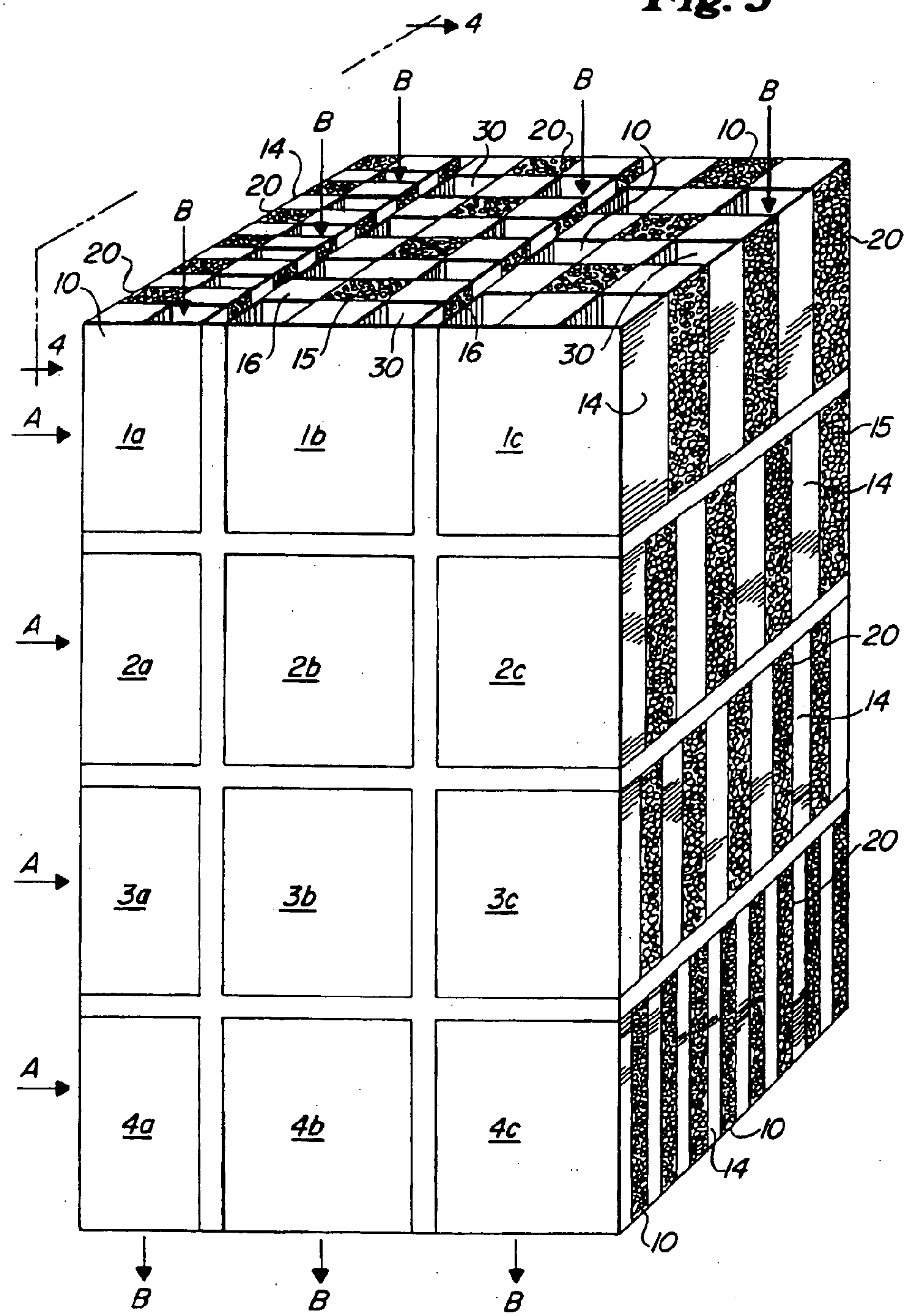

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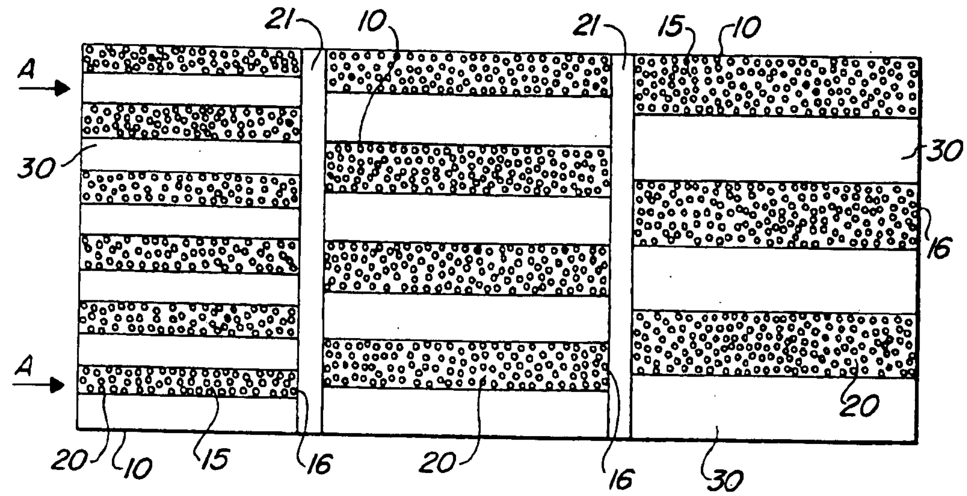
Fig. 4



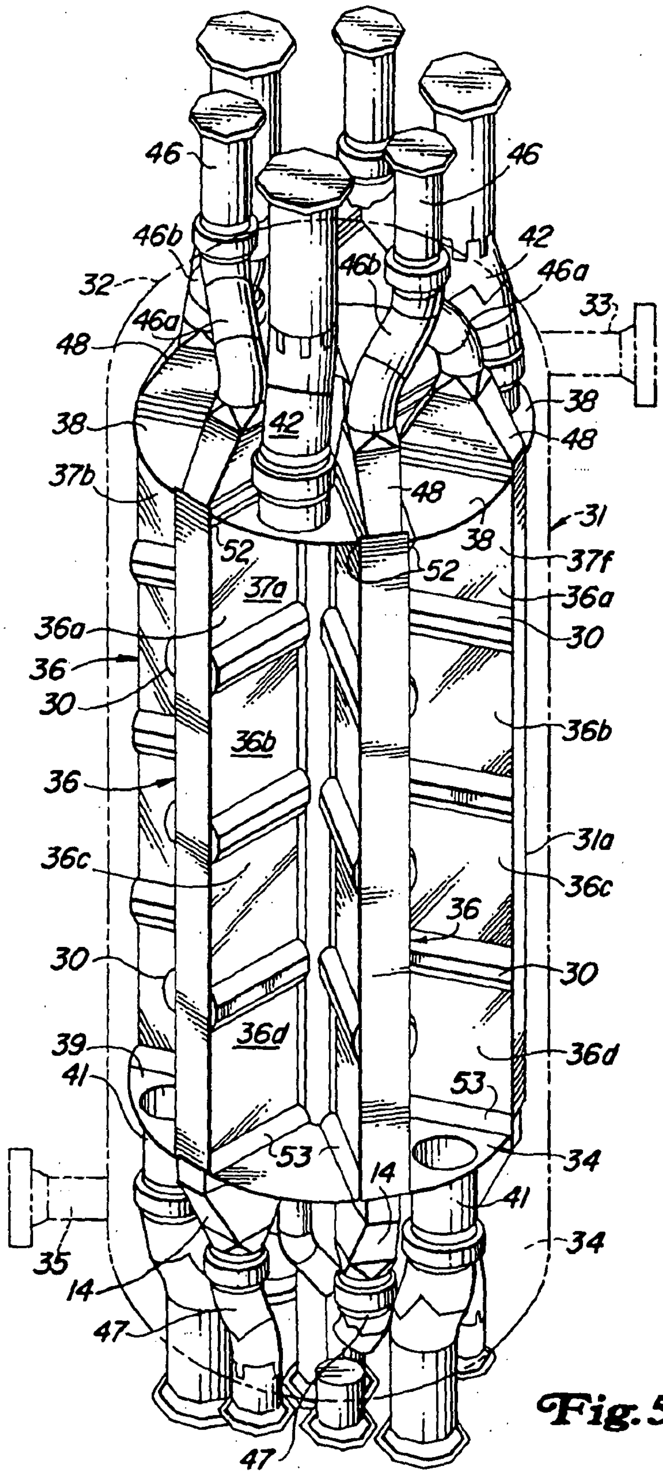

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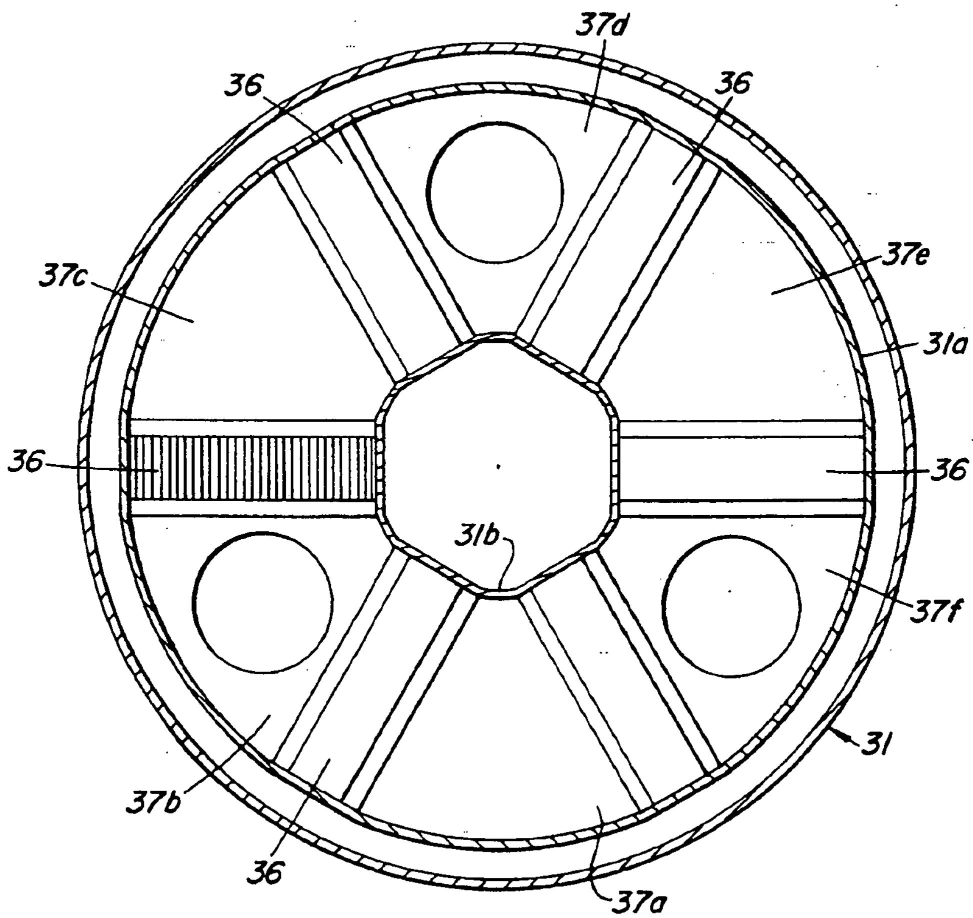
Fig. 5



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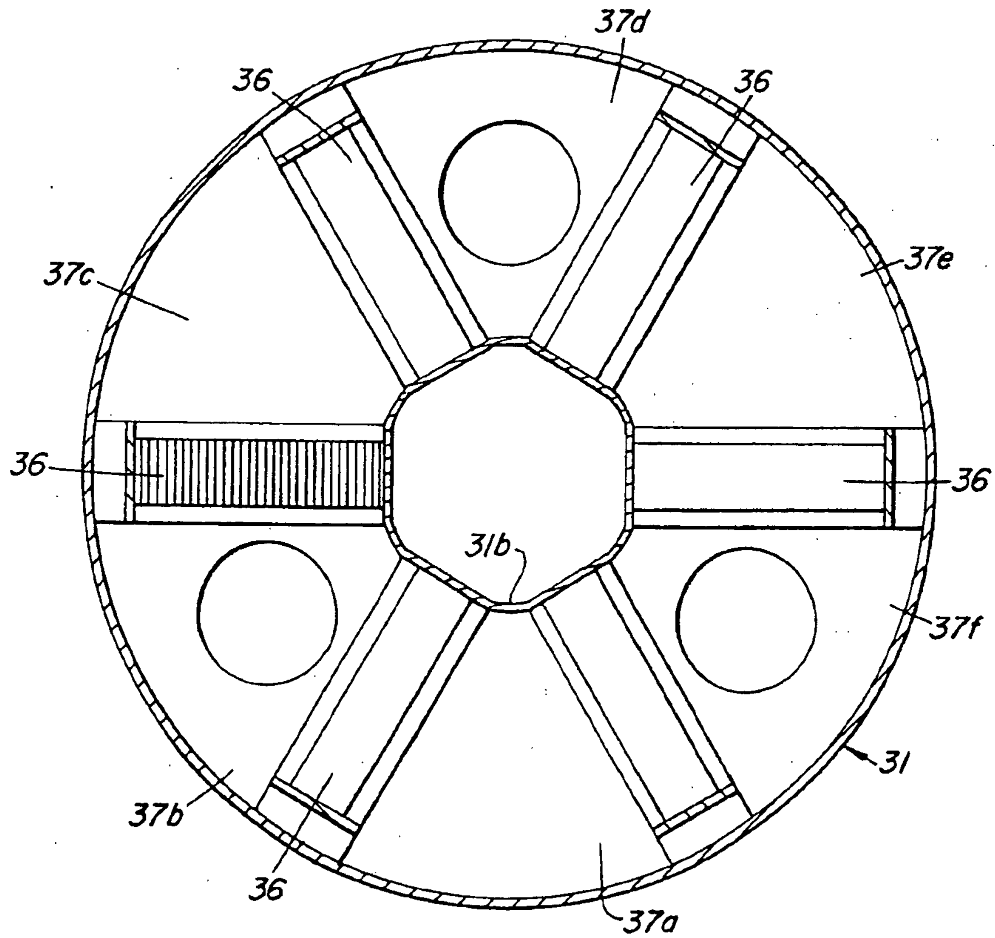

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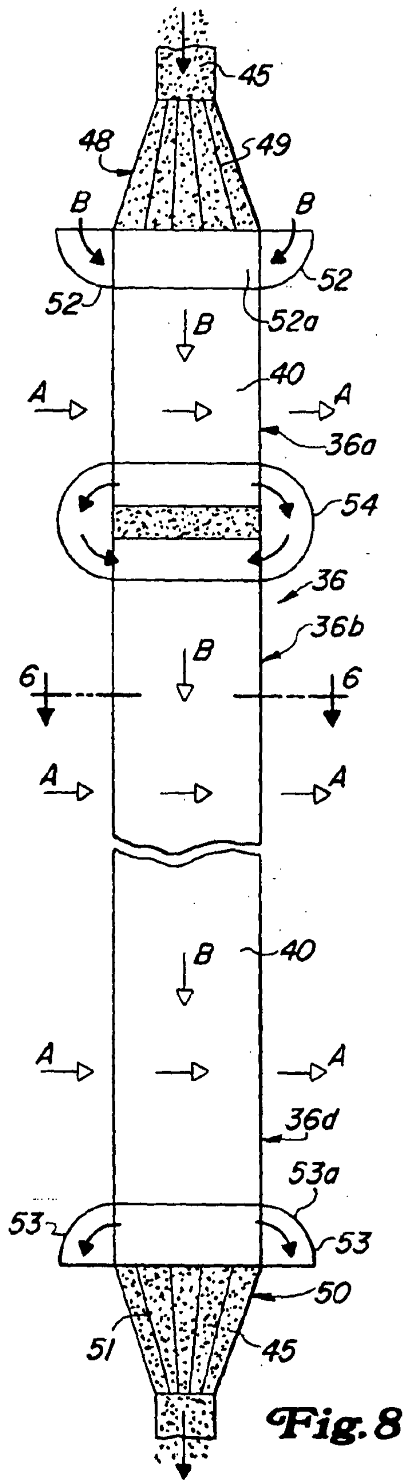
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Fig. 8

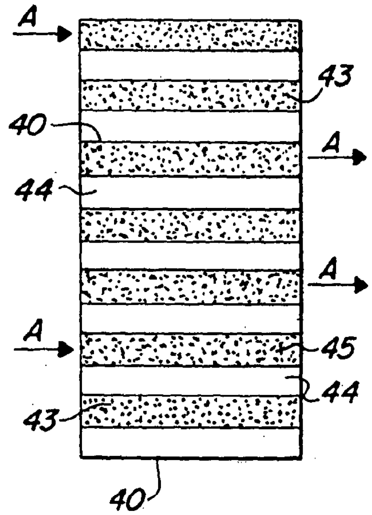
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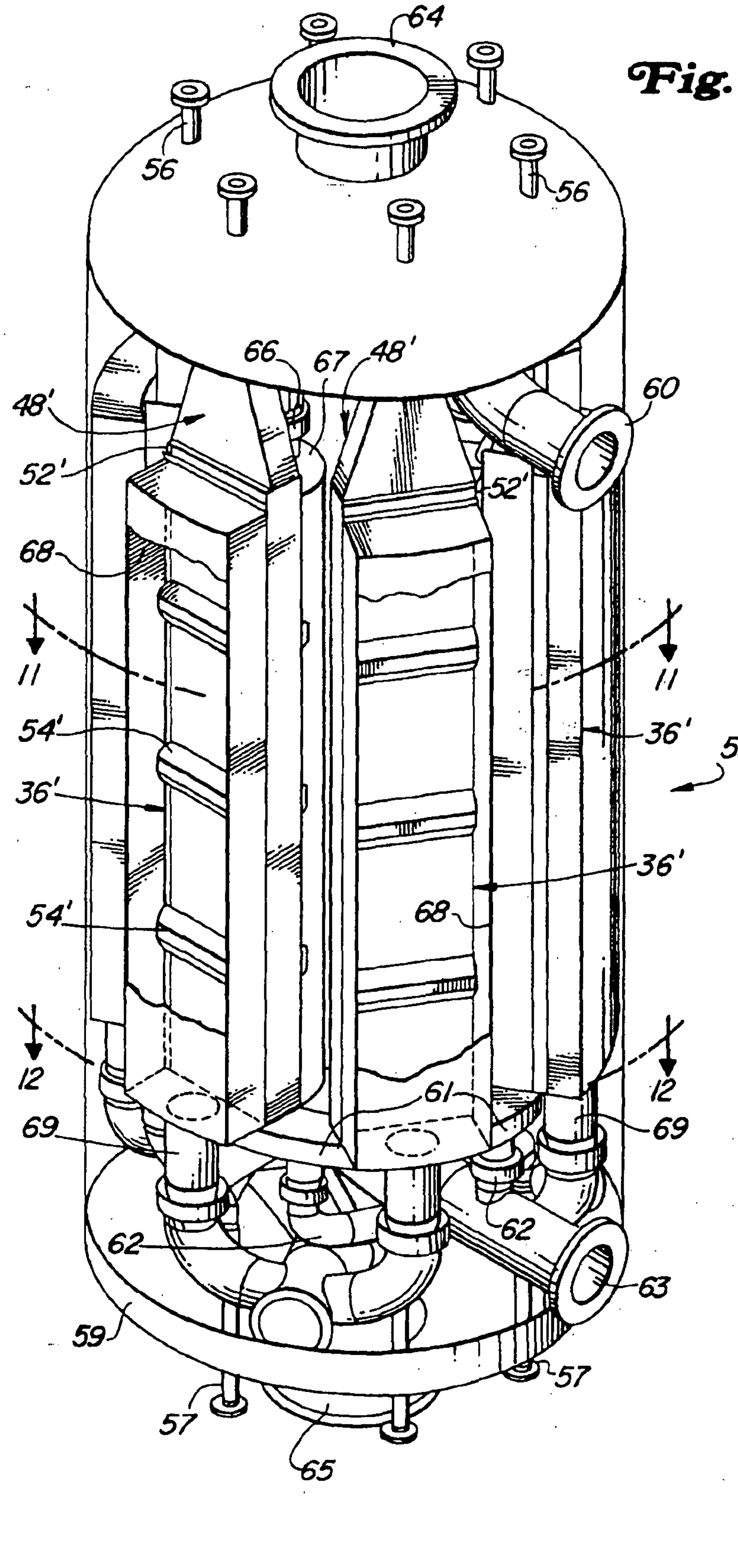
Fig. 9

Fig. 10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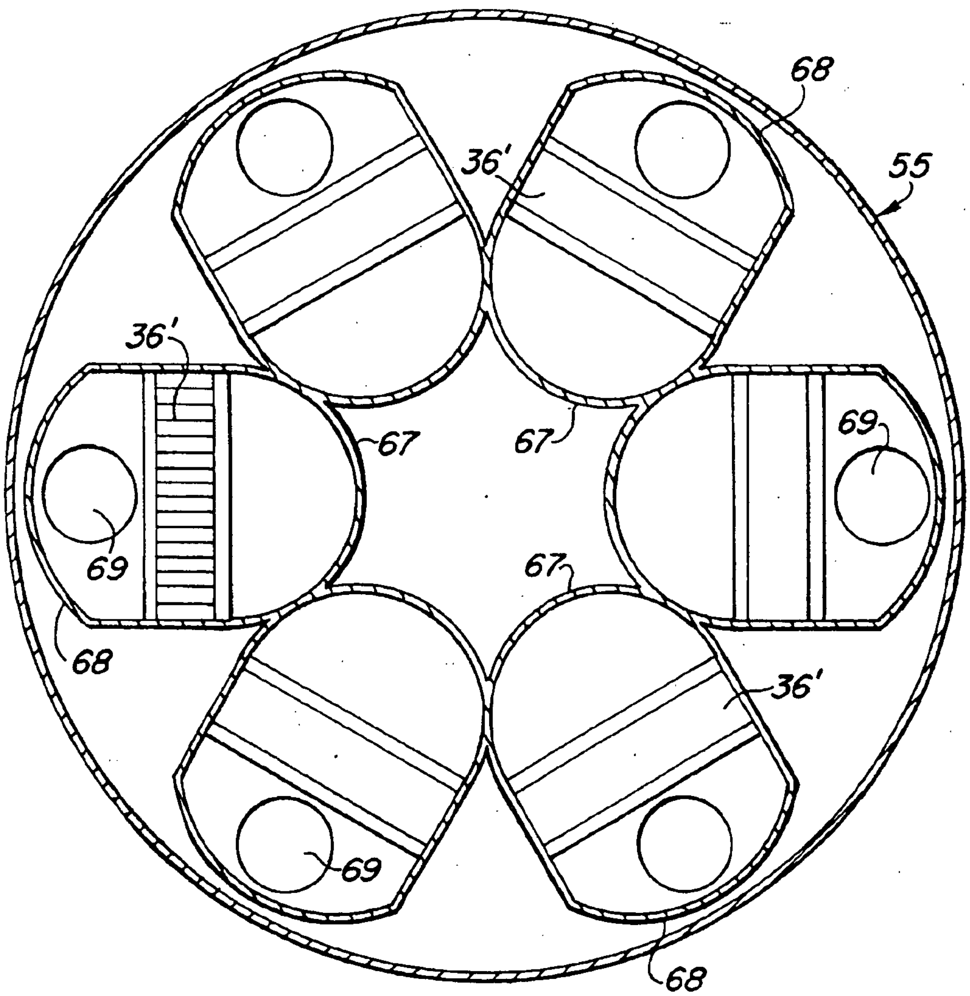

Fig. 11

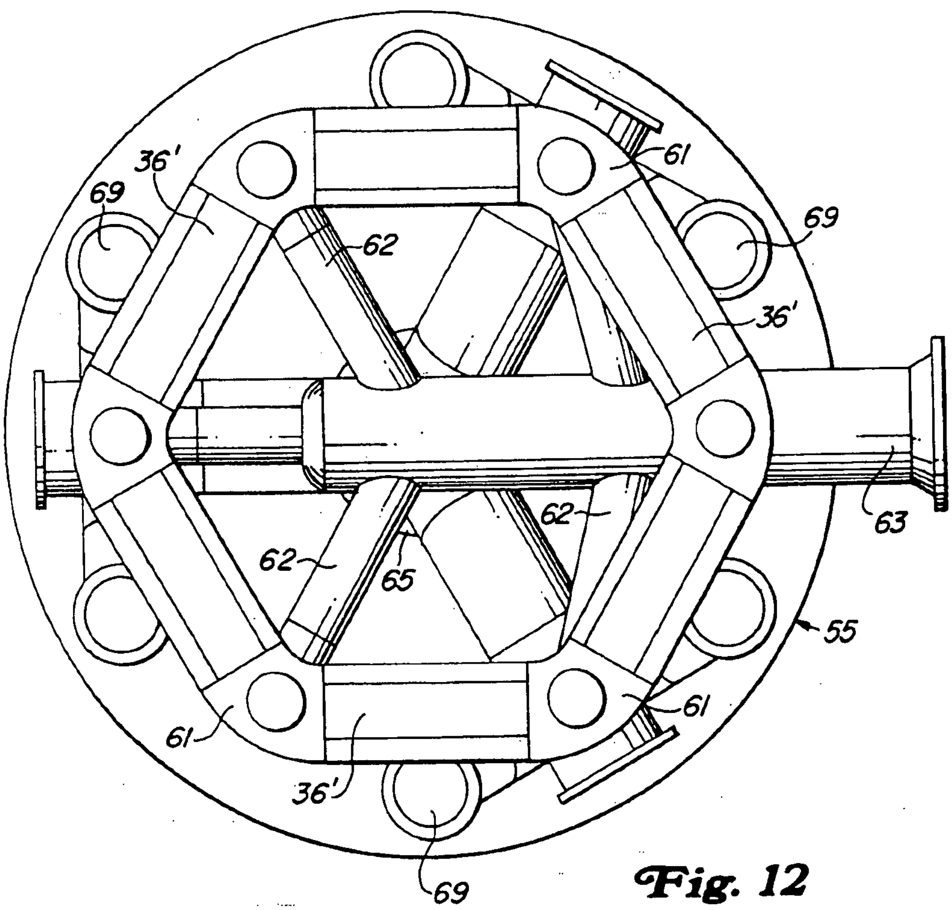

Fig. 12

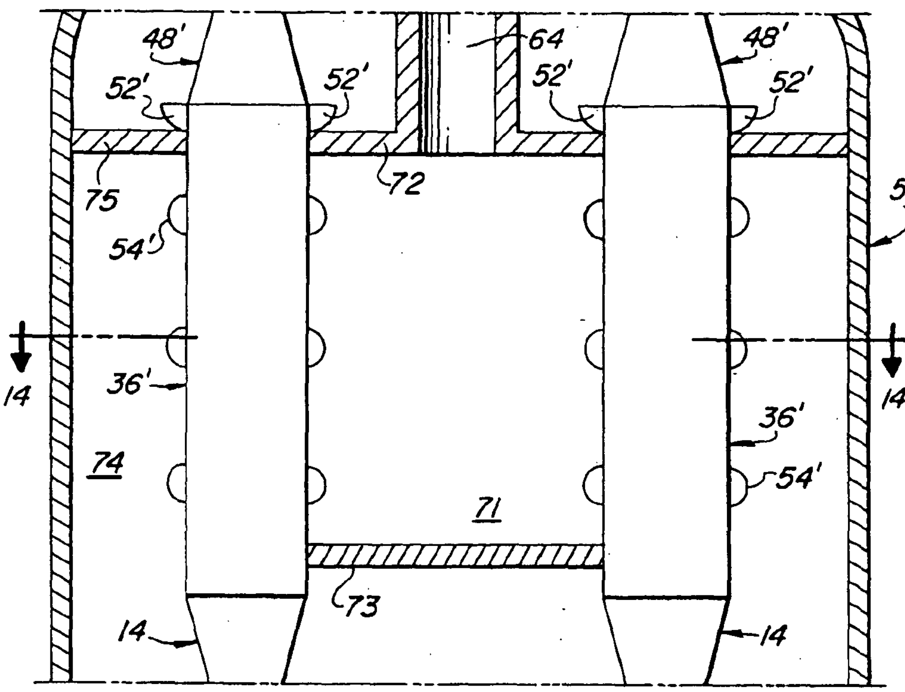
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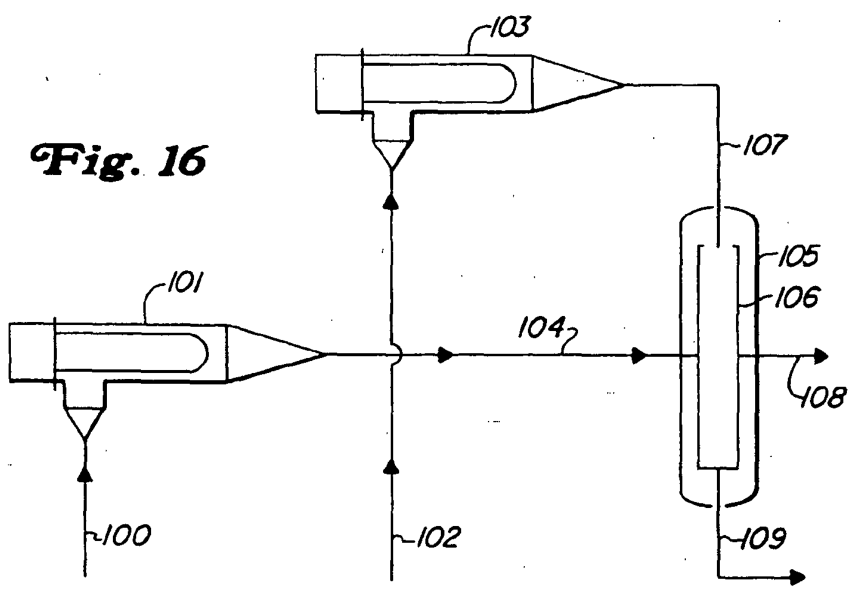
Fig. 13

Fig. 16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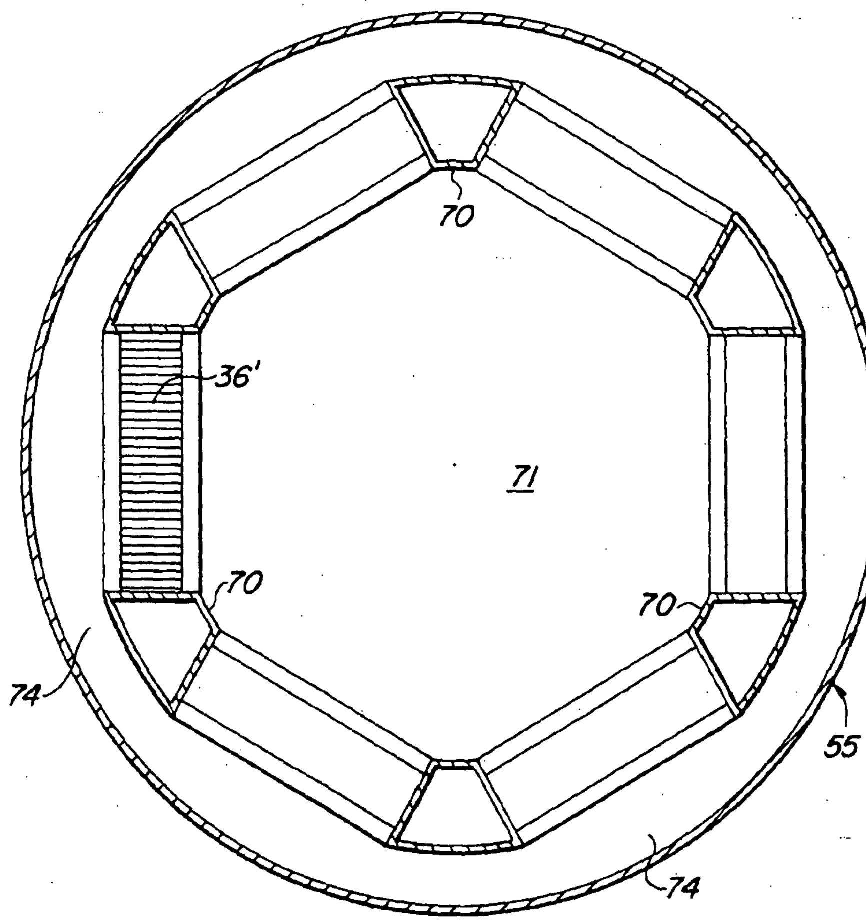

Fig. 14

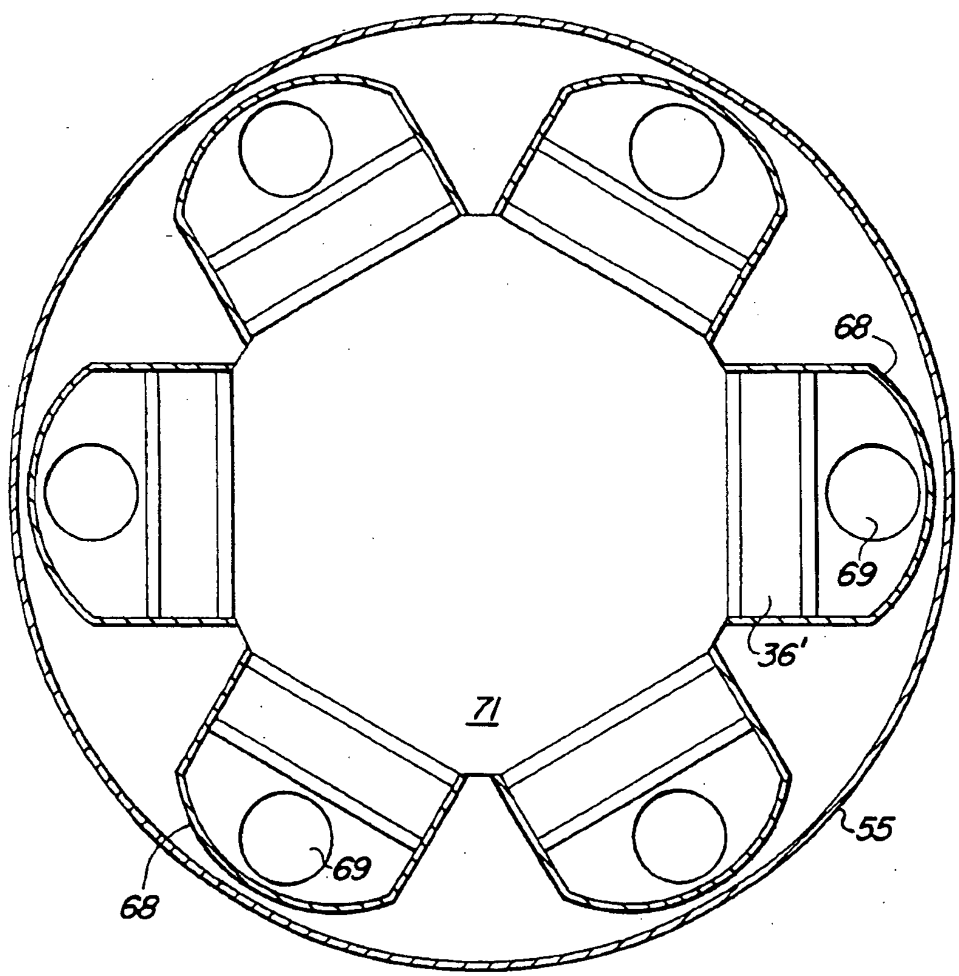

Fig. 15

PROCESS AND APPARATUS FOR CONTROLLING REACTION TEMPERATURES

FIELD OF THE INVENTION

This invention relates to chemical reactors for the conversion of a reaction fluid while indirectly exchanging heat with a heat exchange fluid.

BACKGROUND OF THE INVENTION

In many industries, like the petrochemical and chemical industries for instance, the processes employ reactors in which chemical reactions are effected in the components of one or more reaction fluids under given temperature and pressure conditions. Many of these reactions generate or absorb heat, to various extents, and are, therefore, exothermic or endothermic. The heating or chilling effects associated with exothermic or endothermic reactions can positively or negatively affect the operation of the reaction zone. The negative effects can include among other things: poor product production, aleactivation of the catalyst, production of unwanted by-products and, in extreme cases, damage to the reaction vessel and associated piping. More typically, the undesired effects associated with temperature changes will reduce the selectivity or yield of products from the reaction zone.

One solution for controlling the changes in temperature associated with the heats of various reactions has been to operate several adiabatic reaction zones with intermediate heating or cooling between the different reaction zones. In each adiabatic reaction stage, all of the heat liberated or absorbed during the reaction is transmitted directly to the reactive fluid and the reactor internals. The degree of heat release and the tolerance for temperature change determines the total number of adiabatic reactor zones required in such arrangements. Each zone or adiabatic stage of reaction adds significantly to the overall cost of such a process due to the equipment expense of adding piping and heaters or coolers for intermediate stages of heat transfer to a reactant that passes through the reaction zones. Therefore the number of adiabatic steps is limited and such systems offer at best a stepwise approach to isothermal or other controlled temperature conditions. Moreover, the breaking up of a reaction zone into a series of reactors with intermediate heating or cooling of reactants, especially interferes with reactor arrangements that have continual addition and withdrawal of catalyst from the reaction zone.

Other solutions to the problem of temperature control under the influence of different heats of reaction have employed direct or indirect heating or cooling within the reaction zone. Direct heating or cooling utilizes a compensating reaction having a directionally different heat requirement that occurs simultaneously with the principal reaction. The counter balancing reaction offsets heat release or heat adsorption from the principal reaction. One of the simplest forms of such an arrangement is an endothermic process that uses oxidation of hydrogen to heat reactants in an endothermic reaction.

Another solution has been the indirect heating of reactants and/or catalysts within a reaction zone with a heating or cooling medium. The most well known catalytic reactors of this type are tubular arrangements that have fixed or moving bed catalysts. The geometry of tubular reactors poses layout constraints that require large reactors or limit throughput.

Indirect heat exchange has also been accomplished using thin plates to define channels that alternately retain catalyst and reactants between a heat transfer fluid for indirectly heating or cooling the reactants and catalysts. Heat exchange plates in these indirect heat exchange reactors can be flat or curved and may have surface variations such as corrugations to increase heat transfer between the heat transfer fluids and the reactants and catalysts. Although the thin heat transfer plates can, to some extent, compensate for the changes in temperature induced by the heat of reaction, the indirect heat transfer arrangements are not able to offer the complete temperature control that would benefit many processes by maintaining a desired temperature profile through a reaction zone.

Many hydrocarbon conversion processes will operate more advantageously by maintaining a temperature profile that differs from that created by the heat of reaction. In many reactions, the most beneficial temperature profile will be obtained by substantially isothermal conditions. In some cases, a temperature profile directionally opposite to the temperature changes associated with the heat of reaction will provide the most beneficial conditions. An example of such a case is in alehydrogenation reactions wherein the selectivity and conversion of the endothermic process is improved by having a rising temperature profile, or reverse temperature gradient through the reaction zone.

A reverse temperature gradient for the purposes of this specification refers to a condition where the change in temperature through a reaction zone is opposite to that driven by the heat input from the reaction. In an endothermic reaction, a reverse temperature gradient would mean that the average temperature of the reactants towards the outlet end of the reaction zone have a higher value than the average temperature of the reactants at the inlet end of the reaction zone. In an opposite manner, a reverse temperature gradient in an exothermic reaction refers to a condition wherein reactants towards the inlet end of the reactor have a higher average temperature than the reactants as they pass toward the outlet end of the reaction section.

It is an object of this invention to provide a reactor that offers greater temperature control of reactants by the indirect heating or cooling of a reaction stream by a heat exchange fluid within a reaction zone.

It is a further object of this invention to provide a process and apparatus used for indirect heat exchange of a reactant stream with a heat exchange stream for controlling the temperature profile through the reaction zone.

Another object of this invention is to provide a process that uses indirect heat exchange with a heat exchange fluid to maintain substantially isothermal conditions or a reverse temperature gradient through a reactor.

It is a yet further object of this invention to provide a reactor arrangement and process that facilitates the continuous transfer of catalyst through a reaction zone that indirectly contacts a reactant stream with a heat exchange fluid.

BRIEF SUMMARY OF THE INVENTION

This invention is a chemical reactor and a process for using a chemical reactor that employs an arrangement of heat exchange plates within the reactor that will maintain reactor temperatures within a desired range during the reaction. Two plate arrangement parameters are varied with the process and reactor arrangement of this invention. The plates used in this reactor arrangement will have corrugations formed over the length of the plate for improving heat

transfer across the plates. One of the plate parameters affected by this invention is the relative geometry of the corrugations over different portions of the plates. The other parameter controlled in accordance with this invention is a variation in the number of channels, also expressed the spacing between heat exchange plates, over the length of a heat exchange zone in a reactor. By varying either or both of these parameters, applicants have discovered that a variety of temperature profiles including substantially isothermal or even reverse temperature gradients can be achieved in a reaction zone.

This invention will permit desired control of temperatures through a reaction zone. Preferably this invention will maintain the desired inlet and outlet temperatures within 10° F. and more preferably within 5° F. of desired temperature difference. Where isothermal conditions are desired the inlet and outlet temperature are equal, such that one requirement of the substantially isothermal conditions described in this invention is that the mean inlet and outlet temperature vary by no more than 10° F. and preferably by no more than 5° F.

A process and catalyst reactor arrangement that uses this invention may use single or multiple reaction zones within a reactor vessel. The advantage of this invention is that the reactor vessel can provide the desired temperature gradient without intermediate withdrawal and recycling of reactants or heat exchange medium between the inlet and outlet of the reactor. The multiple reaction zones within the reactor vessel can be used to accommodate variations in the depth or pitch angle of the corrugations in the heat exchange plates or changes in the number of heat exchange plates that define the flow channels of the invention.

Accordingly, in an apparatus embodiment, this invention is a reactor for controlling temperature profiles in a reaction zone. The reactor has a plurality of spaced apart plates with each plate having an extended length and defining a boundary of a heat exchange flow channel on one side of the plate and a boundary of a reaction flow channel on an opposite side of the plate. Each plate defines first corrugations having a first depth and a first pitch angle in a first portion of the plate and defines second corrugations in a second portion of the plate. The first plate portion is spaced away from the second portion along the length of the plates. The second corrugations have a second depth and second pitch angle wherein at least one of the second depth and pitch angle varies from the first depth and pitch angle. The apparatus includes means for passing a reaction fluid along a first flow path through a plurality of the reaction flow channels defined by the plates. The apparatus can also include means for contacting the reaction fluid with a catalyst. The invention also includes a means for passing a heat exchange fluid through a plurality of the reaction flow channels defined by the plates along a second flow path.

The primary control parameter of this invention that allows each individual reaction zone to operate at or near a desired temperature profile is a variation in the pitch angle of the corrugations. Heat transfer enhancement provided by corrugations in the thin plates increases as the corrugations become transverse to the flow of the heat exchange fluid. For example, in the case of an endothermic reaction, arranging the corrugations in a more parallel fashion with respect to the heat transfer fluid at the inlet of the reaction zone and the corrugations in a more transverse fashion toward the outlet end of the reaction zone will provide less heat transfer from the heat transfer fluid at the inlet side than at the outlet side of the reaction zone. In this manner, the increased heat transfer of the corrugations toward the outlet of the reaction zone compensates for loss in temperature of the heat exchange fluid as it passes through the reaction zone. The pitch angle of the corrugations may also be varied to compensate for any increasing heat requirements necessitated by the stage of reaction within the reaction zone. In this manner the variation in corrugation pitch allows the single pass of heat transfer fluid to maintain a desired temperature profile despite any loss of heat transfer fluid temperature as it passes through the reaction zone. In more complex arrangements, it may also be possible to alter the heat transfer coefficient along the length of the reaction zone by changing the depth of the corrugations. However, the simplest and primary means for controlling the temperature within the reaction zone is by varying the pitch angle of the corrugations from more parallel to more transverse with respect to the heat exchange fluid flow.

Changes in heat transfer fluid temperature may be further offset by varying the number of flow channels in different reaction sections of a single plate exchanger reaction arrangement. For a given cross sectional flow area, increasing the number of flow channels decreases the space or gap between plates, increases the number of plates and increases heat transfer. By increasing the number of flow channels, the plate exchange surface area is increased relative to other reaction sections to achieve a more complete approach to the maximum temperature of the heat transfer fluid. Application of the flow channel variation to an endothermic reaction would pass the heating fluid into a reactor and into a first reaction section having plates defining a first number of flow channels. For the purposes of this description a reaction section refers to an arrangement of plates defining a fixed number of spaces between the plates. The heating fluid would then flow out of a first reaction section into a redistribution manifold and then into a second reaction section having a greater number of plates that define an increased number of flow channels for the heating fluid and for the reactants. In such an arrangement, the combination of pitch angle variations in the corrugations of each reaction section would maintain the desired temperature profile within each reaction section and the increase in the number of plates or flow channels will maintain overall average temperatures from reaction section to reaction section within a single system of reaction sections. Both of these effects will allow temperature conditions within a process to be beneficially controlled.

Accordingly, in a process embodiment, this invention is a process for controlling the temperature of a reactant stream in a chemical reaction by indirect heat exchange with a heat exchange fluid across a multiplicity of plate elements. The process passes a heat exchange fluid from a heat exchange inlet to a heat exchange outlet through a first set of elongated channels formed by a first side of the plates. The process also passes a reactant stream from a reactant inlet to a reactant outlet through a second set of channels formed by a second side of the plates. The reactant stream may contact a catalyst in the second set of channels. The process exchanges heat between the heat exchange fluid and the reactant stream by contacting at least the reactant or the heat exchange fluid with corrugations formed by the plates and having a pitch, pitch angle, or corrugation depth adjacent to the reactant inlet or the heat exchange inlet that differs from the pitch, pitch angle or corrugation depth adjacent to the heat exchange outlet or the reactant outlet.

The process may be useful in a wide variety of catalytic reactions. This invention is most beneficially applied to catalytic conversion process having high heats of reaction. Typical reactions of this type are hydrocarbon conversion

reactions that include: the aromatization of hydrocarbons, the reforming of hydrocarbons, the dehydrogenation of hydrocarbons, and the alkylation of hydrocarbons. Specific hydrocarbon conversion processes to which this invention are suited include: catalytic dehydrogenation of paraffins, reforming of naphtha feed streams, aromatization of light hydrocarbons and the alkylation of aromatic hydrocarbons.

The reaction zones for the process of this invention may indirectly contact the reactants with the heat exchange fluid in any relative direction. Thus, the flow channels and inlet and outlets of the reaction zones may be designed for cocurrent, countercurrent, or cross-flow of reactant and heat exchange fluid. Preferred process arrangements for practicing this invention will pass reactants in cross-flow to the heat exchange fluid. Cross-flow of reactants is generally preferred to minimize the pressure drop associated with the flow of reactants through the reactor. For this reason, a cross-flow arrangement can be used to provide the reactants with a shorter flow path across the reaction zone.

The shorter flow path, particularly in the case of the reactant stream contacting heterogeneous catalysts, reduces overall pressure drop of the reactants as they pass through the reactor. Lower pressure drops can have a two-fold advantage in the processing of many reactant streams. Increased flow resistance i.e., pressure drop, can raise the overly operating pressure of a process. In many cases, product yield or selectivity is favored by lower operating pressure so that minimizing pressure drop will also provide a greater yield of desired products. In addition, higher pressure drop raises the overall utility and cost of operating a process.

It is also not necessary to the practice of this invention that each reactant channel be alternated with a heat exchange channel. Possible configurations of the reaction section may place two or more heat exchange channels between each reactant channel to reduce the pressure drop on the heat exchange medium side. When used for this purpose, a plate separating adjacent heat exchange channels may contain perforations.

Additional embodiments, arrangements, and details of the invention are disclosed in the following detailed description of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic representation of a catalytic reaction section of this invention showing a preferred direction for the circulation of fluids and catalyst.

FIG. 2 is a schematic front view of a plate that forms a portion of the channels in the catalytic reaction section of this invention.

FIG. 3 is a schematic exploded view of a catalytic reactor arranged in accordance with this invention.

FIG. 4 is a sectional view taken at section 4—4 of FIG. 3.

FIG. 5 is a diagrammatic perspective view of a catalytic reactor of this invention with a star shaped arrangement of reactor stacks.

FIG. 6 is a transverse section view of the reactor arrangement represented in FIG. 5.

FIG. 7 is a transverse section view of an alternate interior arrangement for the reactor of FIG. 5.

FIG. 8 is a diagrammatic elevation view of a typical catalytic reaction stack forming the star shaped arrangement of FIG. 5.

FIG. 9 is a sectional view along the line 6—6 of FIG. 8.

FIG. 10 is a diagrammatic perspective view of a catalytic reactor of this invention with a polygonally shaped arrangement of reactor stocks.

FIG. 11 is a section view along the line 11—11 of FIG. 10.

FIG. 12 is a section view along the line 12—12 of FIG. 10.

FIG. 13 is a partial diagrammatic elevation view of an alternate reaction stack arrangement according to this invention.

FIG. 14 is a section view along the line 14—14 of FIG. 13.

FIG. 15 is a transverse section view of another polygonal reactor arrangement according to the invention.

FIG. 16 is a process flow diagram of a dehydrogenation process according to the invention.

DETAILED DESCRIPTION OF THE INVENTION

By its very design, the reactor according to this invention has the advantage of maintaining, with simple means, desired temperature profiles including isothermal or reverse gradient temperature conditions during the flow of the reactive fluid in the reactor, by means of a heat transfer medium.

The process and reactor arrangement may use homogeneous or heterogeneous catalysts. Homogeneous catalyst will typically comprise liquid catalysts that flow through reaction channels along with the reactants and are separated for recovery and recycle outside of the reaction zone. This reactor arrangement provides particular benefits with heterogeneous catalysts that are typically retained within the reactant channels by the corrugated plates and permeable members that retain the catalyst but permit the flow of reactants therethrough. In most cases, the heterogeneous catalyst will comprise particulate material retained between the plates and the reactor may be arranged to permit the continuous addition and withdrawal of particulate material while the reactor is on stream.

The type and details of the reactor arrangements contemplated in the practice of this invention is best appreciated by a reference to the drawings. FIG. 1 is a schematic representation of a catalytic reactor section designed to effect a catalytic reaction on a reactant fluid while using indirect heat exchange with a heat transfer fluid to maintain favorable reaction temperatures as the reactant fluid flows through the reaction section. To this end, the catalytic reaction section comprises a stack of parallel plates 10 of the type represented in FIG. 2. Each plate 10 has a central part 12 that forms inclined corrugations 13. Preferably each plate 10 will also contain smooth edges 11 that facilitate the assembly of multiple plates into channels. Referring again to FIG. 1, each plate 10 is stacked next to adjacent plates 10 to form two circulation systems, the first one A for a flow of a reactive fluid and the second one B for flow of an auxiliary fluid. Together FIGS. 1 and 2 define specific circulation systems A and B, wherein the reactive fluid and the heat exchange fluid respectively, flow in crosswise directions, i.e. perpendicular and through alternate channels formed between adjacent plates 10.

Suitable plates for this invention will comprise any plates allowing a high heat transfer rate and which are readily formed into a stable corrugated pattern. The plates may be formed into curves or other configurations, but flat plates are

generally preferred for stacking purposes. Thin plates are preferred and typically have a thickness of from 1 to 2 mm. The plates are typically composed of ferrous or non-ferrous alloys such as stainless steels.

Referring again to FIG. 2 variation in the corrugation arrangement is a preferred method for controlling the temperature profile. The plate arrangement for FIG. 2 represents a typical corrugation pattern for an exothermic or endothermic process. In order to maintain a substantially isothermal or rising temperature profile in such a preferred arrangement the heat transfer fluid flows downwardly through the corrugations on one side of the plate and the reactant stream flows horizontally across the plate on an opposite side. At the upper inlet end the pitch angle of the corrugations is small, i.e. the principle direction of the corrugations approach a parallel alignment with the heat exchange fluid flow. At the lower end of the plate where the heat exchange fluid exits, the pitch angle of the corrugations is wide to increase relative heat transfer, i.e. the principle direction of the corrugations approach a perpendicular or transverse alignment with respect to the heat exchange fluid flow. Corrugation pitch angles can be in a range of from greater than 0° to less than 90° degrees. Typically the corrugation pitch angle from an inlet to an outlet section of a plate will range from about 10° to 80°, and more typically in a range of about 15° to 60°. In a particularly preferred arrangement, the plates will make an angle of less than 30° at the inlet end of the plate and an angle of more than 35° at the outlet end of the plate. The varying corrugations may be formed in a continuous plate section or the plate section of the type shown in FIG. 2 may be made from several plates having corrugations at different pitch angles.

The corrugated plates may be spaced apart or positioned against adjacent plates to form the alternate flow channels. Narrow spacing between the plates is preferred to maximize heat transfer surface. Preferably the corrugation pattern will be reversed between adjacent plates in a reactor section. In this manner the general herring bone pattern on the faces of opposing corrugated plates will extend in opposite directions and the opposing plate faces may be placed in contact with each other to form the flow channels and provide structural support to the plate sections.

Preferably system A, in which the reactant fluid circulates, includes a heterogenous catalyst in the form of particles. The catalyst particles typically comprise grains of a small size. The particles may take on any kind of shape, but usually comprise small spheres or cylinders.

In addition, for the purpose of catalyst loading and unloading, the catalytic reactor may include means for passing catalyst through the metant channels. FIG. 1 shows such means 31, schematically represented, for distributing catalyst in the channels of system A, and in its lower part, means 32, schematically represented, for collecting catalyst during replacement operations.

FIGS. 3 and 4 represent a highly schematic reactor arrangement of the invention showing a generalized arrangement of plates assembled into alternate channels. (In order to simplify the drawing the corrugations have not been shown.) For this purpose, spacers 14 are attached, as represented in FIG. 3, by a suitable method such as welding along the sides of plates 10 to form channels 20, which are open along opposite vertical sides the reactor arrangement for the flow of reactant fluid as shown by arrows A (system A), and channels 30, which are open at the top and bottom of the reactor arrangement for the flow of heat exchange fluid as shown by the arrows B (system B).

When flowing through particle containing channels 20 of system A, the reactant fluid undergoes a catalytic reaction accompanied by a liberation or an absorption of heat. The function of the heat exchange fluid circulating in system B is to convey the heat to be added to or removed from the reactive fluid, in order to maintain favorable reaction conditions. Such conditions can again include isothermal conditions during the circulation of the afore-mentioned reactive fluid in the catalytic reactor or a reverse temperature gradient. The heat exchange fluid is either a gas or a liquid, depending on the specific operating conditions of each process.

The specific heat transfer relationship for the plate exchange is established by the fundamental equation expressing heat transfer between two fluids. This relationship is as follows:

$$P=hxSxLMTD$$

where:

P is the mount of heat exchanged, h is the local or overall heat transfer coefficient, S is the heat exchange area between fluids, and LMTD is the logarithmic mean temperature difference.

The logarithmic mean temperature difference is readily determined by the desired temperature difference at any point along the plate.

For a series of corrugated plates defining alternate channels of catalyst particles and heat exchanger fluid, the local or overall heat transfer coefficient can be calculated by using the following equation:

$$h=f(a,e,dp)$$

where a is the pitch angle of the corrugations, e is the distance between two plates 10, and dp is the equivalent diameter of catalyst particles.

Appropriate values of h can be established by modeling or computed using known correlations for establishing heat transfer coefficients over corrugated surfaces and, where present, through particle beds. Correlations for localized heat transfer through particle beds may be found in Leva, Ind. Eng. Chem., 42, 2498 (1950). Correlations for heat transfer along corrugations are presented in AIChE Symposium Series No. 295 Vol. 89 Heat Transfer Atlanta (1993).

The area of exchange between the reactive fluid and the auxiliary fluid can be calculated by using the equation:

$$S=\epsilon xnxlxL$$

where: ε is a correction factor for the elongation of the plates resulting from the corrugations, n is the number of plates in contact with both heating and reactant fluids, l is the plate width, and L is the plate length.

By varying the number of plates and the characteristics of the corrugations, especially the pitch angle of the corrugations, the invention provides means for maintaining desired temperature conditions in the reactant fluid flow direction.

As shown in the embodiment of FIG. 3, the means for controlling and maintaining temperature conditions consists of having distinct sections 1*a*, 1*b*, 1*c*, 2*a* . . . 4*b*, 4*c* of heat exchange between the reactant fluid circulating in system A and the heat exchange fluid circulating in system B. In FIG. 3, the distinct heat exchange sections 1*a*, 1*b*, 1*c*, 2*a* . . . 4*b*, 4*c* are distributed in the reactant fluid flow direction and in

the heat exchange fluid flow direction, so as to form rows 1, 2, 3, and 4, and columns a, b, and c. In other arrangements of this invention, these distinct heat exchange sections can be distributed solely in the reactant fluid flow direction or solely in the heat exchange fluid flow direction. The total number of distinct reaction sections defined in the entire catalytic reactor of FIG. 3 is obtained by multiplying the number of rows 1, 2, 3 and 4 by the number of columns a, b and c. All the heat exchange sections of a particular row have the same vertical height and all the heat exchange sections of a particular column have the same horizontal width.

Varying the number of plates **10** as represented in FIGS. 3 and 4 increases the heat exchange in the higher numbered rows or lowered lettered columns by adding heat exchange areas between the reactant fluid and the heat exchange fluid in each of the afore-mentioned sections. To obtain a variation of heat exchange within sections **1***a*, **1***b*, **1***c*, **2***a*, **2***b* . . . **4***b*, **4***c*, this invention modifies each of these sections by preferably varying the pitch angle of the corrugations. As represented in FIG. 2, the pitch angle of the corrugations **13** can be more parallel in relation to the reactant fluid flow direction where a high transfer coefficient is required, and more transverse to the fluid flow direction in the heat exchange areas where a low transfer coefficient is required.

The number of plates **10** can increase or decrease from the entry to the exit of the reactive fluid. FIG. 4 shows, as an example, a variation of heat exchange sections from a large number to a small number of plates **10** along the flow path of the reactive fluid.

Where the invention uses a heterogeneous catalyst, the catalytic reactor includes means for containing catalyst **15** in the channels **20** of the reactive fluid circulation system A. As shown in FIGS. 3 and 4, the catalyst containing means can consist of grids **16** placed on either side of channels **20** in each heat exchange area **1***a*, **1***b*, **1***c*, **2***a* . . . **4***b*, **4***c*. These grids **16** cover the whole width of channels **20**, and the mesh size of each grid is inferior to the catalyst **15** grain size.

In addition, where the catalytic reactor of this invention uses a multiplicity of distinct heat exchange sections (**1***a*, **1***b*, **1***c*, **2***a*. . . **4***b*, **4***c*), means for mixing and distributing the reactive and/or the heat exchange fluid are provided. As shown in FIG. 4, these means consist of connecting distribution spaces **21** located between the afore-mentioned heat exchange areas.

FIGS. 5 and 6 diagrammatically show a more specific embodiment of a complete reactor arranged according to this invention. The reactor contains multiple reaction stacks with each stack containing multiple reaction sections. The reactor effects catalytic reaction of a horizontally flowing reactant fluid under controlled temperature conditions, by indirect contact with a vertically flowing heat transfer fluid while permitting movement of catalyst through the reaction stacks.

The reactor comprises a vessel, of circular cross section, designated in its entirety by the reference **31** and shown by the dot-dash lines in FIG. 5. The vessel **31** includes a head **32**, for example of hemispherical shape, on which emerges a nozzle **33** for supplying heat exchange fluid, and a bottom head **34**, for example of hemispherical shape, on which emerges a nozzle **35** for outlet of the heat exchange fluid.

As shown in FIG. 6, the catalytic unit includes two concentric walls **31***a* and **31***b* which are arranged inside vessel **31** and between which walls are arranged reaction stacks **36**. Reaction stacks **36** are vertical and distributed in a star configuration between walls **31***a* and **31***b* of vessel **31**. FIG. 7 shows a variation of FIG. 6 wherein vessel **31** constitutes outer wall **31***a*. The number of reaction stacks **36** is preferably an even number and, in FIGS. 5–7, is equal to six.

The sides of reaction stacks **36** define a portion of feed zones **37***a*, **37***c* and **37***e* arranged alternately between stacks **36** for distributing the reactive fluid and a portion of recovery zones **37***b*, **37***d* and **37***f* arranged alternately between stacks for recovering the reactive fluid. Upper parts of the zones **37***a*, **37***b* . . . **37***f* are blocked off by horizontal plates **38**, each arranged between the reaction stacks **36**, and the lower parts of the zones **37***a*, **37***b* . . . **37***f* are blocked off by horizontal plates **39**, each arranged between the reaction stacks **36**. The star arrangement gives each zone **37***a*, **37***b* . . . **37***f* a triangular prismatic shape, with one of the apexes oriented towards the inside of the vessel **36**. In other embodiments, not shown, each zone **37***a* . . . **37***f* may be divided by a vertical wall into two half-zones with the subdivided parts of the zones providing one feed zone and one recovery zone.

The feed zones **37***a*, **37***c*, and **37***e* are joined to means for inlet of the reaction fluid, which in one form comprises pipes **42**, and the recovery zones **37***b*, **37***d* and **37***f* are joined to means for discharging this reaction fluid which in one form comprise pipes **41**.

As shown in FIGS. 8 and 9, each reaction stack **36** comprises a plurality of parallel plates **40**. The plates **40** are arranged perpendicular to the radius of the vessel **31** and extend downwardly through each of the reaction stacks **36**. Each plate **40** forms, together with the adjacent plates **40**, the previously described circulation circuits A and B. Channels **43** contain horizontal flow through circuit A for the passage of the reactant fluid and channels **44** contain vertical flow through circuit B for the passage of the heat transfer fluid. The circuit A for circulation of the reactive fluid again contains a particulate catalyst **45**. The reactor contains means for passing catalyst into the circuit A of each reaction stack **36** and means for withdrawing catalyst from the circuit A of each reaction stack **36**. As shown in the specific arrangement of FIG. 5, catalyst feed pipes **46**, the number of which is equal to half the number of reaction stacks **36**, receive fresh catalyst particles. Each pipe **46** is divided into two sub-pipes **46***a* and **46***b*, that deliver catalyst particles to the upper part of reaction stack **20**.

A plurality of catalyst discharge pipes **47** are each connected with a lower part of each reaction stack **36**. Pipes **47** pass directly out of vessel **31** to improve catalyst removal. Catalyst particles may be removed from the reactor either periodically or continuously and returned to the reactor stacks after regeneration.

FIGS. 5 and 8 show a diffuser **48** in the upper part of each reaction stack for distributing catalyst into circuit A and a collector **50** at the bottom of stacks **36** for withdrawing catalyst. Diffusers **48** may be fitted with internal baffles or corrugations **13** for distributing the catalyst. Each collector **50** includes internal baffles or corrugations **51** to regulate the flow of the said catalyst into pipe **47**.

Each reaction stack **36** includes, in its upper part, at least one inlet for receiving the heat exchange fluid into circuit B. The inlet may be a single opening. FIGS. 5 and 8 show reaction stack **36** having the inlet in the form of two lateral bowl shaped inlets **52** each arranged on opposite sides of the corresponding reaction stack **36**. Inlet **52** opens to the interior of vessel **31**, which contains the heat exchange fluid from fluid nozzle **33**. The heat exchange fluid is introduced into circuit B from inlet **52** by a distribution zone **52***a*.

Each reaction stack **36** also typically includes, in its lower part, at least one collector for recovering the heat exchange fluid at the outlet of the circuit B. FIGS. 5 and 8 show each

reaction stack 36 having two lateral collectors 53, each arranged on one side of the reaction stack 36 to receive heat transfer fluid from a recovery zone 53a that communicates with channels 44. The collectors communicate, via the open portion of the vessel 31 below plate 39, with the outlet nozzle 35 for withdrawing the heat exchange fluid.

The embodiment shown in FIGS. 5–9 shows each reaction stack 36 divided into a plurality of reaction sections 36a, 36b, 36c and 36d which are joined together by intermediate connecting zones 54. Connecting zones 30 serve as redistribution manifolds to permit the segregated passage of the heat exchange fluid and the catalyst between the various reaction sections 36a, 36b, 36c and 36d.

A typical mode of operation passes reactant fluid, heat exchange fluid and, optionally, catalyst through the reactor 31. Reactant fluid enters reactor 31 via the pipes 42, passes into the feed zones 37a, 37c and 37e, then passes horizontally through two adjacent reaction stacks 36 via the circuit A and emerges in the recovery zones 37b, 37d and 37f. Pipes 41 subsequently discharge the reactant fluid. The heat exchange fluid enters the upper part of the vessel 31 via the nozzle 33, passes into the reactor stacks 36 via the inlet zones 52 and the distribution zone 52a. The heat exchange fluid passes vertically through the reactor stacks 36 via the circuit B and exits the reaction stack 36 via the recovery zones 53a and the collectors 53. The heat exchange fluid emerges into the lower part of the vessel 31 and exits via the nozzle 35. Catalyst 45 enters circuit A of each reaction stack 36 via the pipes 46, the sub-pipes 46a and 46b and the diffuser 48 wherein the reactive fluid contacts the catalyst in the circuit A. Collectors 50 and pipes 47 periodically or continuously withdraw catalyst from the bottom of reaction stack 36.

In order to maintain the desired temperature profiles while the reactant fluid passes through the catalyst of each reaction section 36a, 36b, 36c and 36d, each section varies the pitch angle of the corrugations defined by plates 40. The number of plates in each successive downwardly located reaction section 36(a–d) increases to progressively add surface area for heat exchange between the reaction fluid and the heat exchange fluid down the length of each reaction stack 36.

Preferably, the reaction stacks 36 are kept under compression within vessel 31 by the heat exchange fluid. The operating pressure of the heat exchange fluid is typically regulated to a value slightly higher than that of the reaction fluid. For this purpose, the heat exchange fluid usually fills the vessel 31 and surrounds the reaction stacks 36.

The vessel 31, may have the reaction stacks 36 located therein in a variety of different arrangements. Another type of arrangement as shown in FIG. 10 places the reaction stacks such that the plates 40 are substantially parallel to the radius of a vessel 55. The arrangements of plates 40 parallel to the radius of vessel 55 provides a generally polygonal configuration for the reaction stacks. The reaction stacks form a substantially circumferential ring within the reactor vessel 55.

In FIGS. 10–12, piping and duct arrangements for the delivery and recovery of reaction fluids, heat exchange fluids, and catalysts are substantially similar to those described for the reactor arrangement of FIGS. 5–9 and all details of the reaction stacks are also substantially similar to those described. Catalyst particles enter the reactor vessel 10 through nozzle 56. Diffusers 48' at the top of reaction stacks 36' transfer the catalyst into the reaction stacks across upper head 58. Nozzles 57 withdraw catalyst from the reactor stacks 36' through a collector of the type previously described and across lower head 59. The heat exchange fluid enters reactor 55 through a nozzle and fills the interior of vessel 55. The heat transfer fluid enters the reaction stacks 36' through an inlet 52' and passes through adjoining reaction sections by connecting zones 54'. Collectors at the bottom of reactor stacks 36' discharge the heat exchange fluid into a collection manifold 61. Pipes 62 withdraw heat exchange fluid from manifold 61. Pipes 63 collects heat exchange fluid from pipes 62 to withdraw the heat exchange fluid from vessel 55. Additional details of manifold 61 and pipes 62 and 63 are shown in FIG. 12. The reaction fluid flows through vessel 55 from an inlet nozzle 64 to an outlet nozzle 65. Nozzle 64 distributes the reaction fluid to multiple distributor pipes 66. Each distributor pipe 66 delivers reaction fluid to a distribution chamber 67. Each distribution chamber 67 covers the side of each reaction stack 36' that faces the interior of the vessel 55. Distribution chambers 67 have a closed bottom that forces the flow of reaction fluid across each reaction stack 36' and into a collector 68 that seals an opposite face of each reaction stack 36'. The upper portion of each collector 68 is closed to direct the exiting flow of reaction fluid into conduits 69 for collection and withdrawal by nozzle 65.

In another embodiment shown in FIGS. 13 and 14, the reactor stacks 36' are connected into a substantially polygon shape and housed by reactor vessel 55. Plates 70 shown in FIG. 14 define an inner distribution space 71 for the reaction fluid. As shown in FIG. 13, an upper baffle 72 and a lower baffle 73 form the upper and lower boundaries of distribution space 71. The reaction fluid enters the distribution space across upper baffle 72 via nozzle 64 and flows from inner distribution space 71 into an outer collection space 74. Outer collection space 74 eliminates the necessity for collection piping and the reaction fluid exits the vessel directly from an open nozzle 65 (not shown). Unlike the previous reactor configurations, the embodiment of FIGS. 13 and 14 shows the reaction fluid surrounding the reaction stacks 36'. A baffle 35, together with baffle 33 isolates the upper portion of vessel 55 to form a distribution chamber for delivery of the heat exchange fluid into inlets 52' in the manner previously described. The heat exchange fluid again exits the reactions stacks 36' through a manifold and piping system to substantially the same as that shown in FIGS. 10–12. Any flow of catalyst practiced in the embodiment of FIGS. 13 and 14 occurs in essentially the same manner as that previously described.

FIG. 15 shows an arrangement for reaction stacks 35' that combines the inlet distribution space of FIG. 13 and 14 with the collection baffles shown in FIGS. 10–12. In the arrangement shown in FIG. 15, any catalyst flow again occurs in the same manner as that previously described. In regard to reaction fluid, it flows into central chamber 71 in the manner associated with FIGS. 13–14 and is collected and withdrawn from the reaction stacks 36' in the manner associated with FIGS. 10–12. With the arrangement of reaction stacks as shown in FIG. 15, the flow of heat exchange fluid through the reactor may be controlled with two different piping and baffling arrangements. The entering heat exchange fluid may surround the reaction stacks 36' and fill the interior of vessel 55 while a manifold system similar to that depicted in FIGS. 10–12 withdraws the effluent heat exchange fluid. In another arrangement, baffles such as those depicted in FIGS. 13 and 14 seal off an upper volume of vessel 55 to distribute incoming heat exchange fluid to inlets 52' while the effluent heat exchange fluid surrounds reaction stacks 36' and is withdrawn from the open lower volume without the use of any manifold or piping system.

Catalytic reforming is a well established hydrocarbon conversion process employed in the petroleum refining

industry for improving the octane quality of hydrocarbon feedstocks, the primary product of reforming being motor gasoline. The art of catalytic reforming is well known and does not require extensive description herein. Briefly, in catalytic reforming, a feedstock is admixed with a recycle stream comprising hydrogen and contacted with catalyst in a reaction zone. The usual feedstock for catalytic reforming is a petroleum fraction known as naphtha and having an initial boiling point of about 180° F. (80° C.) and an end boiling point of about 400° F. (205° C.). The catalytic reforming process is particularly applicable to the treatment of straight run gasoline comprised of relatively large concentrations of naphthenic and substantially straight chain paraffinic hydrocarbons, which are subject to aromatization through dehydrogenation and/or cyclization reactions. Reforming may be defined as the total effect produced by dehydrogenation of cyclohexanes and dehydroisomerization of alkylcyclopentanes to yield aromatics, dehydrogenation of paraffins to yield olefins, dehydrocyclization of paraffins and olefins to yield aromatics, isomerization of n-paraffins, isomerization of alkylcycloparaffins to yield cyclohexanes, isomerization of substituted aromatics, and hydrocracking of paraffins. Further information on reforming processes may be found in, for example, U.S. Pat. No. 4,119,526 (Peters et at.); U.S. Pat. No. 4,409,095 (Peters); and U.S. Pat. No. 4,440,626 (Winter et at), the contents of which are herein incorporated by reference.

A catalytic reforming reaction is normally effected in the presence of catalyst particles comprised of one or more Group VIII noble metals (e.g., platinum, iridium, rhodium, palladium) and a halogen combined with a porous carrier, such as a refractory inorganic oxide. The halogen is normally chlorine. Alumina is a commonly used carrier. The preferred alumina materials are known as the gamma, eta and the theta alumina with gamma and eta alumina giving the best results. An important property related to the performance of the catalyst is the surface area of the carrier. Preferably, the carrier will have a surface area of from 100 to about 500 m^2/g. The particles are usually spheroidal and have a diameter of from about 1/16th to about 1/8th inch (1.5–3.1 mm), though they may be as large as 1/4th inch (6.35 mm). A preferred catalyst particle diameter is 1/16th inch (3.1 mm). During the course of a reforming reaction, catalyst particles become deactivated as a result of mechanisms such as the deposition of coke on the particles; that is, after a period of time in use, the ability of catalyst particles to promote reforming reactions decreases to the point that the catalyst is no longer useful. The catalyst must be reconditioned, or regenerated, before it can be reused in a reforming process.

In preferred form, the reforming operation will employ a moving bed reaction zone and regeneration zone. The present invention is applicable to moving bed and fixed bed zones. In a moving bed operation, fresh catalyst particles are fed to a reaction zone by gravity. Catalyst is withdrawn from the bottom of the reaction zone and transported to a regeneration zone where a multi-step regeneration process is used to recondition the catalyst to restore its full reaction promoting ability. Catalyst flows by gravity through the various regeneration steps and then is withdrawn from the regeneration zone and furnished to the reaction zone. Movement of catalyst through the zones is often referred to as continuous though, in practice, it is semi-continuous. By semi-continuous movement is meant the repeated transfer of relatively small amounts of catalyst at closely spaced points in time. A moving bed system has the advantage of maintaining production while the catalyst is removed or replaced.

Another preferred hydrocarbon conversion process is the alkylation of aromatic hydrocarbons. In aromatic alkylation suitable aromatic feed hydrocarbons for this invention include various aromatic substrates. Such substrates can be benzene or alkylated aromatic hydrocarbons such as toluene. The acyclic feed hydrocarbon or alkylating agent that may be used in the alkylation reaction zone also encompasses a broad range of hydrocarbons. Suitable alkylating agents include monoolefins, diolefins, polyolefins, acetylenic hydrocarbons and other substituted hydrocarbons but are preferably C_2–C_4 hydrocarbons. In the most preferred form of this invention, the alkylation agent will comprise C_2–C_4 monoolefins.

A wide variety of catalysts can be used in the alkylation reaction zone. The preferred catalyst for use in this invention is a zeolite catalyst. The catalyst of this invention will usually be used in combination with a refractory inorganic oxide binder. Preferred binders are alumina or silica. Preferred alkylation catalysts are a type Y zeolite having an alumina or silica binder or a beta zeolite having an alumina or silica binder. The zeolite will be present in an amount of at least 50 wt. % of the catalyst and more preferably in an amount of at least 70 wt. % of the catalyst.

The alkylation reaction zone can operate under a broad range of operating conditions. Temperatures usually range from 100° C. to 325° C. with the range of about 150°–275° C. being preferred. Pressures can also vary within a wide range of about 1 atmosphere to 130 atmospheres. Since liquid phase conditions are generally preferred within the reaction zone, the pressure should be sufficient to maintain the reactants in such phase and will typically fall in a range of from 10 to 50 atmospheres. Reactants generally pass through the alkylation zone at a mass flow rate sufficient to yield a liquid hourly space velocity from 0.5 to 50 hrs^{-1} and especially from about 1 to 10 hrs^{-1}.

The alkylation zone is ordinarily operated to obtain an essentially complete conversion of the alkylating agent to monoalkylate and polyalkylate. To achieve this effect, additional aromatic substrate will usually be charged to the reaction zone. Thus, the feed mixtures are introduced into the reaction zone at a constant rate and a molecular ratio of about 1:1 to 20:1 aromatic substrate to alkylating agent with a ration of about 2:1 to 10:1 being preferred. As a result, in addition to product there will usually be a substantial amount of unreacted aromatic substrate that is removed with the product stream from the alkylation reaction zone. Additional details of aromatic alkylation processes can be found in U.S. Pat. No. 5,177,285, the contents of which are hereby incorporated by reference.

Catalytic dehydrogenation is another example of an endothermic process that advantageously uses the process and apparatus of this invention. Briefly, in catalytic dehydrogenation, a feedstock is admixed with a recycle stream comprising hydrogen and contacted with catalyst in a reaction zone. Feedstocks for catalytic dehydrogenation are typically petroleum fractions comprising paraffins having from about 3 to about 18 carbon atoms. Particular feedstocks will usually contain light or heavy paraffins. For example a usual feedstock for producing a heavy dehydrogenation products will comprise paraffins having 10 or more carbon atoms. The catalytic dehydrogenation process is particularly applicable to the treatment of hydrocarbon feedstocks containing substantially paraffinic hydrocarbons which are subject to dehydrogenation reactions to thereby form olefinic hydrocarbon compounds.

A catalytic dehydrogenation reaction is normally effected in the presence of catalyst particles comprised of one or

more Group VIII noble metals (e.g., platinum, iridium, rhodium, palladium) combined with a porous carrier, such as a refractory inorganic oxide. Alumina is a commonly used carrier. The preferred alumina materials are known as the gamma, eta and theta alumina with gamma and eta alumina giving the best results. Preferably, the carrier will have a surface area of from 100 to about 500 m^2/g. The particles are usually spheroidal and have a diameter of from about 1/16th to about 1/_th inch (1.5–3.1 mm), though they may be as large as ¼th inch (6.35 mm). Generally, the catalyst particles have a chloride concentration of between 0.5 and 3 weight percent. During the course of a dehydrogenation reaction, catalyst particles also become deactivated as a result of coke deposition and require regeneration, similar to that described in conjunction with the reforming process; therefore, in preferred form, the dehydrogenation process will again employ a moving bed reaction zone and regeneration zone.

Dehydrogenation conditions include a temperature of from about 400° to about 900° C., a pressure of from about 0.01 to 10 atmospheres and a liquid hourly space velocity (LHSV) of from about 0.1 to 100 hr^{-1}. Generally, for normal paraffins, the lower the molecular weight the higher the temperature required for comparable conversions. The pressure in the dehydrogenation zone is maintained as low as practicable, consistent with equipment limitations, to maximize the chemical equilibrium advantages. The preferred dehydrogenation conditions of the process of this invention include a temperature of from about 400°–700° C., a pressure from about 0.1 to 5 atmospheres, and a liquid hourly space velocity of from about 0.1 to 100 hr^{-1}.

The effluent stream from the dehydrogenation zone generally will contain unconverted dehydrogenatable hydrocarbons, hydrogen and the products of dehydrogenation reactions. This effluent stream is typically cooled and passed to a hydrogen separation zone to separate a hydrogen-rich vapor phase from a hydrocarbon-rich liquid phase. Generally, the hydrocarbon-rich liquid phase is further separated by means of either a suitable selective adsorbent, a selective solvent, a selective reaction or reactions or by means of a suitable fractionation scheme. Unconverted dehydrogenatable hydrocarbons are recovered and may be recycled to the dehydrogenation zone. Products of the dehydrogenation reactions are recovered as final products or as intermediate products in the preparation of other compounds.

The dehydrogenatable hydrocarbons may be admixed with a diluent gas before, while, or after being passed to the dehydrogenation zone. The diluent material may be hydrogen, steam, methane, carbon dioxide, nitrogen, argon and the like or a mixture thereof. Hydrogen is the preferred diluent. Ordinarily, when a diluent gas is utilized as the diluent, it is utilized in amounts sufficient to ensure a diluent gas to hydrocarbon mole ratio of about 0.1 to about 20, with best results being obtained when the mole ratio range is about 0.5 to 10. The diluent hydrogen stream passed to the dehydrogenation zone will typically be recycled hydrogen separated from the effluent from the dehydrogenation zone in the hydrogen separation zone.

Water or a material which decomposes at dehydrogenation conditions to form water such as an alcohol, aldehyde, ether or ketone, for example, may be added to the dehydrogenation zone, either continuously or intermittently, in an amount to provide, calculated on the basis of equivalent water, about 1 to about 20,000 weight ppm of the hydrocarbon feed stream. About 1 to about 10,000 weight ppm of water addition gives best results when dehydrogenating paraffins having from 6 to 30 more carbon atoms. Additional information related to the operation of dehydrogenation catalysts, operating conditions, and process arrangements can be found in U.S. Pat. Nos. 4,677,237; 4,880,764 and 5,087,792, the contents of which are hereby incorporated by reference.

EXAMPLE

The effect of using the process and reactor arrangements of this invention to maintain isothermal conditions was investigated in a hydrocarbon conversion process for the dehydrogenation of paraffins. A simulation based on the ability of this invention to maintain isothermal conditions was prepared based on a feedstream having a composition given in Table 1. The isothermal conditions that result from this invention were simulated in a dehydrogenation process as depicted in FIG. **16**.

In this process simulation, a feedstream carried via line **100** and having the composition given in Table 1 passes into a heater **101** that raises the feedstream temperature from approximately 600° F. to 850° F. At the same time, a heat exchange medium having the same relative composition as feedstream **100** is carried via line **102** into a heater **103**. Heater **103** raises the temperature of the heat exchange fluid to approximately 890° F.

A line **104** carries the heated feedstream into a reactor **105** that directs the feedstream into a heat exchange bundle **106** designed in accordance with this invention. Reactor **105** has an arrangement to pass the feedstream through a circuit A containing a typical dehydrogenation catalyst comprising platinum on an alumina support. A line **107** carries the heat exchange fluid from heater **103** into reactor **105** which passes the heat exchange medium downwardly through the heat exchange bundle **106** in the manner previously described in relation to circuit B. The process simulation of reactor bundle **106** is based on the use of a heat exchange bundle **106** having three layers of catalyst, a vertical height of about 1.5 m, and a width of about 100 mm. The plates defining the channels which alternate between catalyst and feedstream and the heat exchange fluid have a thickness of about 1.2 mm, corrugations with a depth of about 10 mm and a width of about 270 mm. The plates are placed next to each other in an alternating pattern of corrugations, such that the peaks of the corrugations are in contact. The reactor operates at an average pressure of about 20 psig in both circuits A and B. The total pressure drop through the system for the reaction fluid is about 2 psi. Indirect heat exchange of the reaction fluid with the heat exchange medium provides an outlet mean temperature of about 850° F.

The convened reactant stream and the heating stream are recovered from the process. The product stream **108** having the composition given in the table is withdrawn from the reactor at a temperature of about 850° F. A line **109** carries the heat exchange medium from the reactor at a temperature of about 870° F. A comparison of process streams **100** and **108** shows the conversion of C_{10} to C_{14} paraffins to corresponding olefins.

TABLE 1

Stream Description lb. mole/hr	100	102	108
Molar Flow	14.7195	15.2562	86.4876
H_2O	0.2044	0.2044	1.3073
Hydrogen	11.0421	11.5787	70.6316
Methane	0.0725	0.0725	0.4637
Ethane	0.1411	0.1411	0.9027
Propane	0.0308	0.0308	0.1968
n-Butane	0.0093	0.0093	0.0592

TABLE 1-continued

Stream Description lb mole/hr	100	102	108
n-Pentane	0.0026	0.0026	0.0165
n-Decane	0.3509	0.3023	1.4082
n-C11	1.4016	1.1810	5.6242
n-C12	1.0262	0.8454	4.1177
n-C13	0.4162	0.3340	1.6701
n-C14	0.0207	0.0161	0.0829
1-Nonene	0.0000	0.0001	0.0000
1-Decene	0.0000	0.0486	0.0000
1-Undecene	0.0000	0.2206	0.0000
1-Dodecene	0.0000	0.1807	0.0000
1-Tridecene	0.0000	0.0822	0.0000
Total:	14.7195	15.256	86.4876

What is claimed is:

1. reactor for controlling temperature profiles in a reaction zone, said reactor comprising:

a) a plurality of spaced apart plates with each plate having a length and defining a boundary of a heat exchange flow channel on one side of said plate and a boundary of a reaction flow channel on an opposite side of said plate and each plate defining first corrugations having a first depth and first pitch angle in a first portion of said plate and defining second corrugations in a second portion of said plate portion spaced along the length of said plates said second corrugations having a second depth and a second pitch angle wherein at least one of said second depth and said second pitch angle varies from said first depth and pitch angle;

b) means for passing a reaction fluid through a plurality of said reaction flow channels defined by said plates along a first flow path; and,

c) means for passing a heat exchange fluid through a plurality of said heat exchange flow channels defined by said plates along a second flow path.

2. The reactor of claim 1 wherein said first flow path is perpendicular to said second flow path.

3. The reactor of claim 1 wherein said plates are discontinuous and said first portion comprises a first plate section and said second portion comprises a second plate section.

4. The reactor of claim 1 wherein said plates are continuous and the pitch angle of said corrugations varies over the length of each plate.

5. The reactor of claim 4 wherein the pitch angle of said corrugations with respect to the heat transfer fluid flow direction makes an angle of less than 30° at an inlet end of said plate and an angle of more than 35° at an outlet end of said plate.

6. The reactor of claim 1 wherein said reactor includes means for retaining catalyst in said reaction flow channels.

7. The catalytic reactor of claim 1 wherein said plates are parallel.

8. The reactor of claim 1 wherein each of said plates in said reactor defines a reactant channel on one face and a heat exchange channel on an opposite face.

9. The reactor of claim 1 wherein each heat exchange channel is divided by a plate having an extended length.

10. A catalytic reactor for controlling temperature profiles in a reaction zone, said reactor comprising:

a) a first plurality of spaced apart plates having a length with each plate defining flow channel boundaries on their opposing sides for defining a first multiplicity of flow channels and each plate defining corrugations having a first pitch angle in a first portion of said plates and a second pitch angle in a second portion of said

plates, wherein said first and second portions are spaced apart along the length of said first plurality of plates;

b) a second plurality of spaced apart plates having a length with each plate defining flow channel boundaries on their opposing sides for defining a second multiplicity of flow channels that vary in number from said first multiplicity of flow channels and each plate defining corrugations having a first pitch angle in a first portion of said second plurality of plates and a second pitch angle in a second portion of said second plurality of plates, wherein said first and second portions are spaced apart along the length of said second plurality of plates;

c) means for retaining catalyst and passing a reaction fluid through a first group of flow channels comprising a first half of the flow channels in said first and second multiplicity of flow channels; and,

d) means for passing a heat exchange fluid through a second group of said flow channels comprising a second half of the flow channels in said first and second multiplicity of flow channels.

11. The catalytic reactor of claim 10 wherein said means for passing said reaction fluid divides said reaction fluid between said first and second plurality of spaced apart plates for parallel flow through said first group of flow channels and said means for passing said heat exchange fluid passes the heat exchange fluid serially through the first and second group of flow channels.

12. The catalytic reactor of claim 10 wherein said means for passing said heat exchange fluid divides said heat exchange fluid between said first and second plurality of spaced apart plates for parallel flow through said second group of flow channels and said means for passing said reaction fluid passes the reaction fluid serially through the first group of flow channels.

13. A catalytic reactor for controlling temperature profiles in a reaction zone, said reactor comprising:

a) a cylindrical vessel;

b) at least two vertically extended reaction stacks located in said vessel containing at least one reaction section, said reaction sections comprising a plurality parallel plates having a vertical length and a spaced apart arrangement to define flow channel boundaries on their opposing sides to define an interleaved multiplicity of horizontal flow channels for horizontal flow of a reaction fluid and vertical flow channels for vertical flow of a heat exchange fluid, each plate defining corrugations and said corrugations having a first pitch angle in a first portion of said plates and a second pitch angle in a second portion of said plates, wherein said first and second portions are spaced apart along the length of said first plurality of plates;

c) means for distributing a heat exchange fluid to the vertical flow channels in each reaction stack and collecting said heat exchange fluid from each of said reaction stacks;

d) means for distributing a reaction fluid to the horizontal flow channels in each reaction stack and collecting said reaction fluid from each of said reaction stacks;

e) means for retaining a catalyst in said horizontal flow channels.

14. The reactor of claim 13 wherein said reactor stacks comprise an upper reaction section and a lower reaction section located directly below said upper reaction section, said upper reaction section and said lower reaction section

contain a different number of plates and said reaction stack includes a connection duct for communicating vertical flow channels between said upper and lower reaction sections.

15. The reactor of claim **14** wherein said connection duct has means for communicating catalyst particles from horizontal flow channels in said upper reaction section to horizontal flow channels in said lower reaction section.

16. The reactor of claim **13** wherein said reactor contains at least three reaction stacks and said reaction stacks are located with the plates parallel to the radius of the vessel to form a polygon configuration.

17. The reactor of claim **16** wherein said reaction stacks surround an interior volume of said reactor to define, at least in part a distributor to provide at least a part of said means for distributing a reaction fluid to said horizontal flow channels.

18. The reactor of claim **13** wherein said reactor contains at least three reaction stacks and said reaction stacks are located with the plates in each reaction stack perpendicular to the radius of said vessel to form a star configuration.

19. The reactor of claim **18** wherein at least two adjacent reaction stacks define two sides of a triangular prismatic volume and said volume provides at least a portion of said means for distributing a reaction fluid to the horizontal flow channels in each reaction stack and collecting said reaction fluid from each of said reaction stacks.

* * * * *

US006334985B1

(12) **United States Patent**
Raghuram et al.

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(45) **Date of Patent: Jan. 1, 2002**

(54) **STATIC MIXING REACTOR FOR UNIFORM REACTANT TEMPERATURES AND CONCENTRATIONS**

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(73) Assignee: **UOP LLC**, Des Plaines, IL (US)

(*) Notice: This patent issued on a continued prosecution application filed under 37 CFR 1.53(d), and is subject to the twenty year patent term provisions of 35 U.S.C. 154(a)(2).

Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **09/135,682**

(22) Filed: **Aug. 18, 1998**

(51) **Int. Cl.**[7] **F28D 3/00**; F28D 7/00; B01F 3/04

(52) **U.S. Cl.** **422/224**; 422/200; 422/228; 165/166; 165/167

(58) **Field of Search** 422/200, 224, 422/228, 312, 198, 189, 201, 191; 165/166, 167, 170, 165; 366/340, 147, 337

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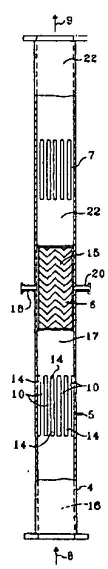
(74) *Attorney, Agent, or Firm*—John G. Tolomei; James C. Paschall

(57) **ABSTRACT**

A tubular reactor passes a flowing stream of reactants through a plurality of mixing devices that simultaneously provide indirect heat exchange of the reactants to improve the uniformity of reactant temperatures and concentrations. The mixing devices provide intimate mixing by passing the reactants through a plurality of narrow channels defined by parallel plate elements that channel a heat exchange fluid on their opposite side to provide the simultaneous indirect heat exchange. The heat exchange channels can have any desired degree of mixing intensity by providing irregularities in the channel walls or flow path that supply the desired degree of fluid shear. Preferably the mixing reactor provides a series of mixing devices with heat exchange along the length of the conduit flow path with space between the devices for remixing of the fluid reactants.

8 Claims, 5 Drawing Sheets



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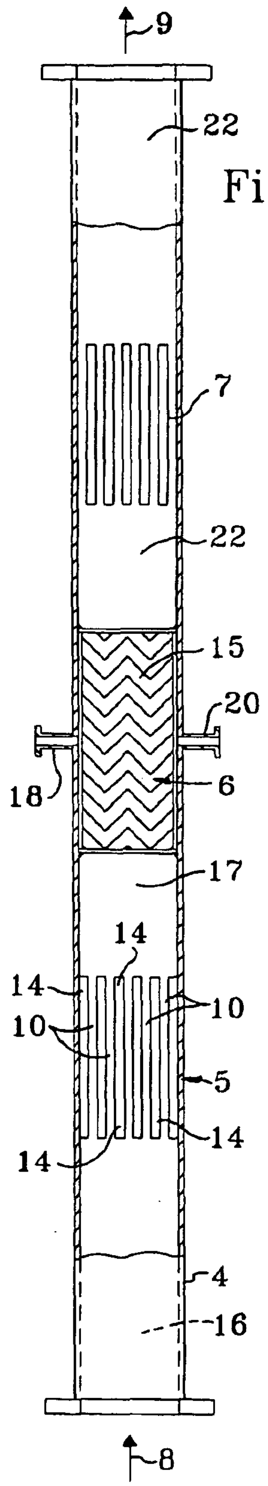
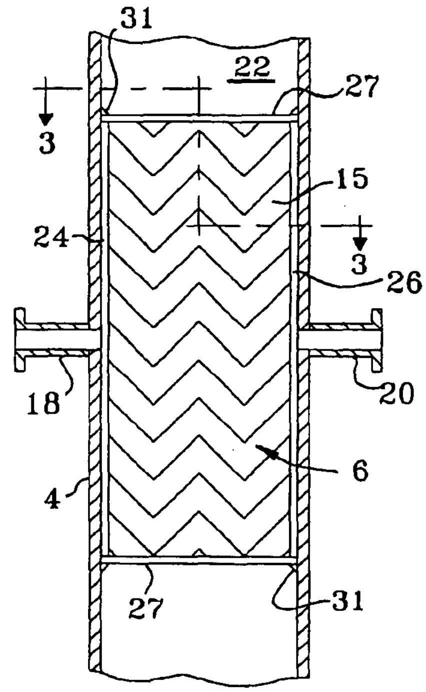


Fig. 1

Fig. 2



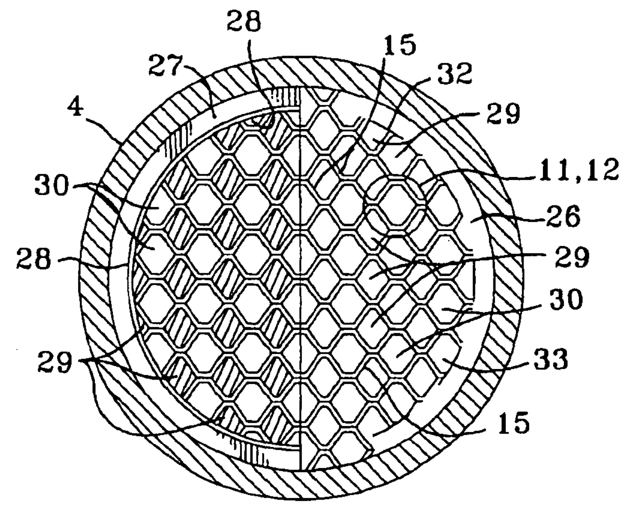


Fig. 3

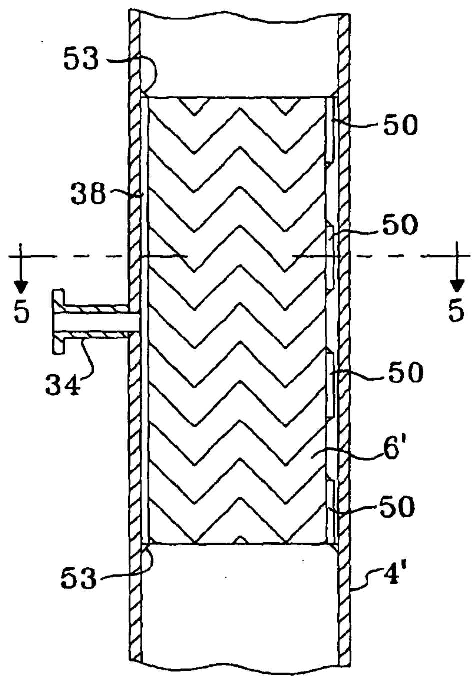

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Fig. 4

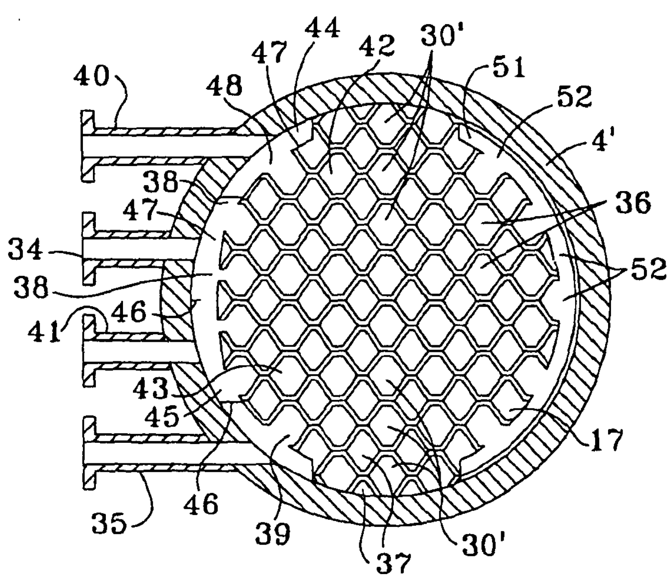
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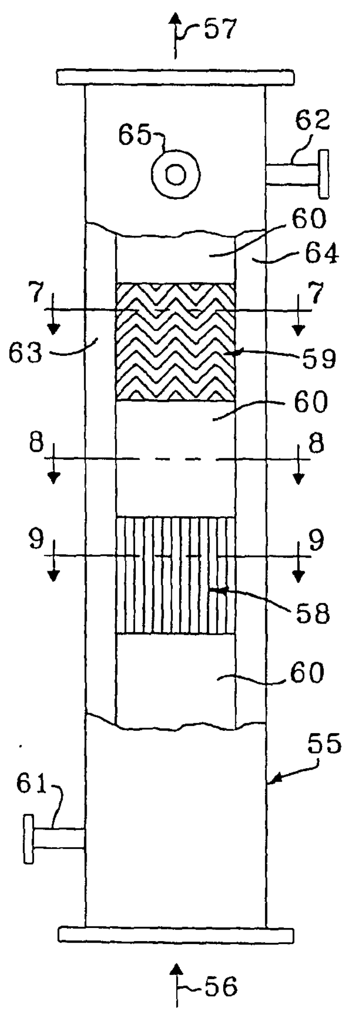
Fig. 5

Fig. 6



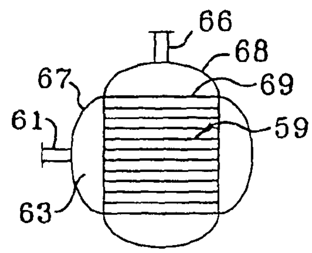


Fig. 7

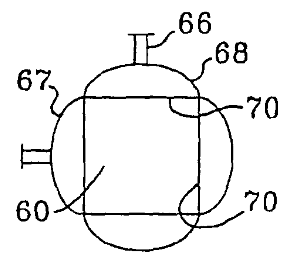


Fig. 8

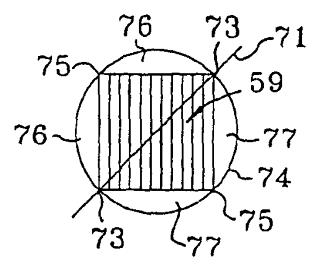


Fig. 9

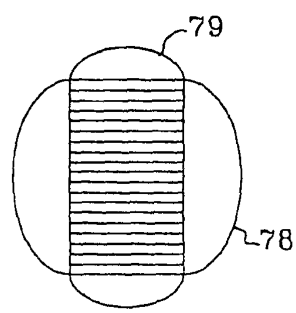


Fig. 10

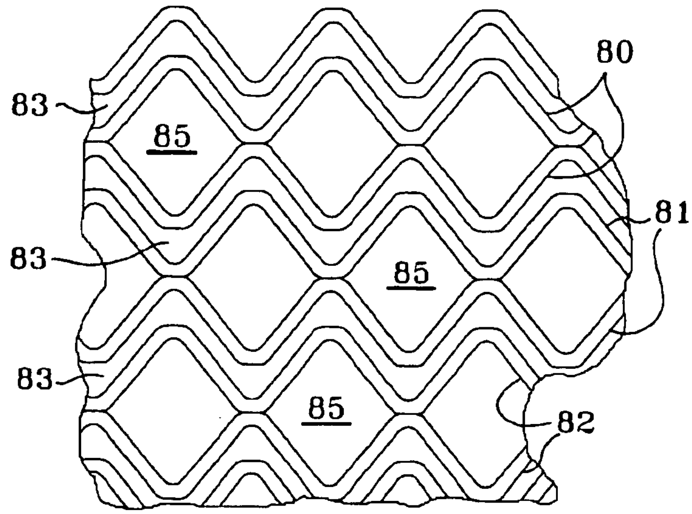


Fig. 11

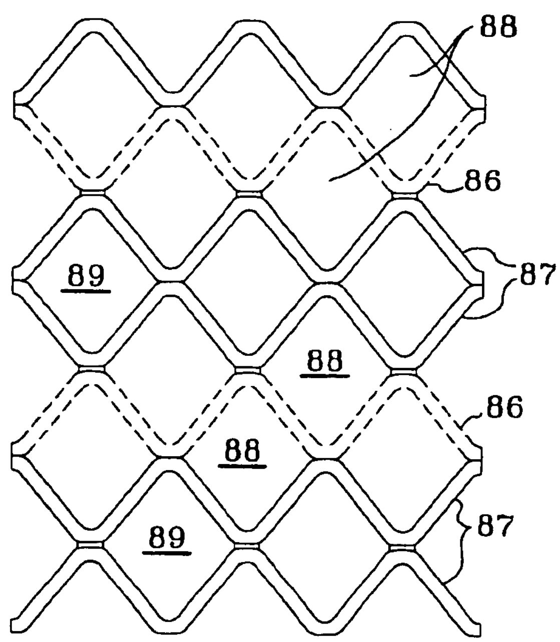


Fig. 12

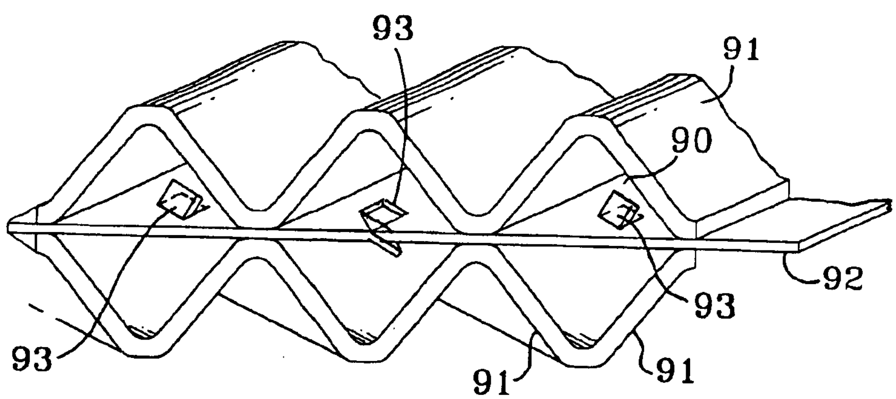


Fig. 13

STATIC MIXING REACTOR FOR UNIFORM REACTANT TEMPERATURES AND CONCENTRATIONS

FIELD OF THE INVENTION

This invention relates to reactor arrangements having means for mixing reactants and to the heating of reactants in such reaction zones.

BACKGROUND OF THE INVENTION

There are many homogenous or heterogeneous chemical reactions involving liquid and/or gas vapor phases that benefit from the intimate mixing of the reactants in the reaction zone.

This intimate mixing is usually supplied by a tubular reactor. These reactors consist of a long conduit into which the reactants are injected. Mixing of the reactants occurs as they flow down the conduit. The design requirements for these reactors include the variables of temperature, degree of mixing and residence time. Direct or indirect heat transfer may be employed to control temperature conditions within the tubular reactor. For example it is known that such reactors may be externally jacketed to circulate a heat exchange medium on the outside surface of an extended reaction conduit and thereby provide indirect heating or cooling over the entire external surface of the reactor.

The primary variables influencing the design of the mixing reactors are the degree of mixing, the residence time, and the temperature of the reaction. The length of the conduit or pipe is usually sized to control residence time. The degree of mixing is largely a function of the flow regime within the conduit. In open tubular reactors the diameter largely controls the flow regime therein. Thus optimal velocity for tubular reactions is established when the pipe diameter correctly keeps the flow in the desired flow regime within a pipe or conduit having a length that provides the proper residence time for the reaction. The temperature depends on the heat of reaction and the degree to which heat may be added or withdrawn via intermediate injection of reactants or diluents and the availability of indirect heat exchange.

External heating and the addition of fluids do not always offer satisfactory temperature control. Since many mixing reactors depend on high fluid velocities through the reaction zone, processes with high heats of reaction may not receive enough heat flux to maintain optimum temperatures without exceeding local temperature limitations for the reactants. The direct addition of heating or cooling fluids may also interfere with process control by varying the velocity and residence time through the reaction zone as well as composition concentrations.

The requirements for mixing and residence time are also not always fully compatible, and therefore, the diameter of the conduit containing a mixing reactor may represent a compromise in optimum values to control mixing and residence time. In addition, many tubular reactors require very long pipe lengths at high velocities to achieve the necessary mixing. One means of overcoming the incompatibility in the flow regime or residence time and long length requirements is the use of internal mixers within a tubular reactor or other reaction zone. Internal mixing devices include stirred reactors and static mixers.

In some cases, conduit or tubes of mixing reactors are also unable to provide the intensity of the mixing that may be important for certain reactions. In order to overcome mass transfer limitations, many reactions that require intimate mixing of reactants also require the mixing be accomplished with a high degree of shear forces between the fluids. The high shear forces create the necessary phase dispersion to overcome mass transfer limitations inherent in the fluids and to provide the contacting necessary for precise reaction control.

Stirred tank reactors in many cases may provide the necessary shear forces to eliminate mass transfer limitations. However, stirred tank reactors often provide unwanted areas of stagnation that allow variations in residence time and degrade the products obtained from certain reactions. In addition, the mechanical elements of stirred tank reactors may prove troublesome. When operating at high pressure, impeller shaft seal leakage is particularly difficult to prevent.

Static mixers are commonly used to supply additional mixing energy to the reactor instead of mechanical stirred reactors. These types of static mixers include simple static mixers, fluidic mixers and vortex mixers. Simple static mixers are effective in forming and dispersing gas bubbles in a statistical distribution.

U.S. Pat. No. 5,409,672 issued to Centinkaya shows a static mixer arrangement provides a high fluid shearing while minimizing pressure drop.

U.S. Pat. No. 5,538,700 issued to Koves shows an arrangement of corrugated plates that use a perforated insert plate to introduce additional turbulence into heat exchange channels.

U.S. Pat. No. 5,525,311 issued to Girod et. al. show a process and arrangement that uses plates to defined a plurality of catalyst retaining channels for processing a reactant stream interleaved with a plurality of channels that receive a heat exchange fluid.

BRIEF SUMMARY OF THE INVENTION

It is an object of this invention to provide a mixing type reactor that can provide intimate mixing and efficient internal heat exchange.

It is a further object of this invention to provide a mixing type reactor that can provide intimate mixing and simultaneous internal heat exchange with a desired degree of fluid shearing.

This invention is a mixing reactor that passes a flowing stream of reactants through a plurality of mixing devices that simultaneously provide indirect heat exchange of the reactants. The mixing devices provide intimate mixing by passing the reactants through a plurality of narrow channels defined by parallel plate elements that channel a heat exchange fluid on their opposite side to provide the simultaneous indirect heat exchange. The heat channels can have any desired degree of mixing intensity by providing irregularities in the channel walls or a flow path that supplies the desired degree of fluid shear. Preferably the mixing reactor provides a series of mixing devices with heat exchange along the length of the conduit flow path with space between the devices for remixing of the fluid reactants. Thus, the degree of stirring required by the reaction can be intensified by the addition of the required number of mixing devices positioned along the flow path through the tube or conduit of the reactor. The additional stages of mixing or shear may be added to continue mixing components as reactants are produced or to maintain dispersion as additional reagents or catalysts are added between stages of mixing or as intermediate fluids are withdrawn from the reactor.

Accordingly, in one embodiment this invention is an apparatus for the plug flow reaction of one or more reactants

in the presence of gas, liquid or mixed phase fluids. The apparatus includes a containment conduit having an inlet and an outlet end for passing fluid from the inlet end to the outlet end and establishing a flow direction through the conduit. At least two spaced apart mixing sections comprising a plurality of spaced apart plates definine heat exchange flow channels and reactant flow channels, the plates retain turbulence inducing structures that extend transversely across the reactant flow channels and the plates define reactant channel inlets for the reactant channels at the upstream end of the mixing sections and define reactant channel outlets for the reactant channels at the end of the mixing section opposite the reactant channel inlets. A distribution manifold for distributes a heat exchange fluid to the sides of the heat exchange channels. A collection manifold for collects a heat exchange fluid from the sides of the heat exchange channels.

In a more specific embodiment this invention comprises an apparatus for the plug flow reaction of one or more reactants in the presence of a gas, a liquid or mixed phase fluids. The apparatus includes at least three chamber conduit sections defining connecting volumes for passing a reactant stream from a contactor inlet, through at least two mixing devices and out of the contactor outlet and establishing a reactant flow path. A plurality of parallel plates, spaced apart in a stacked arrangement, form a plurality of reactant flow channels interleaved with a plurality of heat exchange channels in each mixing device and provide each mixing device with a rectilinear profile transverse to the reactant flow path. The plates retain turbulence inducing structures that extend transversely into the reactant flow channels. The plates define reactant channel inlets for the reactant channels at the upstream end of the mixing device and reactant channel outlets for the reactant channels at the end of the mixing device opposite the reactant channel inlets. The plates define a heat exchange inlet on one side of the heat exchange channels and a heat exchange outlet on the opposite side of the heat exchange channels. A first curved containment section having a concave side defines a distribution manifold over the heat exchange inlet side of each mixing device for distributing a heat exchange fluid to the sides of the heat exchange channels. A second curved containment section having a concave side defining a collection manifold over the heat exchange outlet side of each mixing device collects a heat exchange fluid from the sides of the heat exchange channels.

Additional objects, embodiments and details of this invention are disclosed in the following detailed description of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates a tubular reactor of this invention and shows the mixing device in a cut-away view.

FIG. 2 is an enlarged cross-section of one of the mixing devices shown in the cut-away view of FIG. 1.

FIG. 3 is a split section of the upper portion of the mixing device shown in FIG. 2 taken over lines 3—3.

FIG. 4 is a modified cross section of the mixing device shown in FIG. 2.

FIG. 5 is a section of FIG. 4 taken at line 5—5.

FIG. 6 is an alternate arrangement for a mixing conduit reactor of this invention.

FIGS. 7 and 8 are sections of FIG. 6 taken at lines 7—7 and 8—8, respectively.

FIG. 9 is a modified cross section of a mixing device taken at line 9—9 of FIG. 6.

FIG. 10 is a modified cross section showing an alternate arrangement for the conduit reactor of FIG. 6.

FIG. 11 is modified arrangement for reactant and heat exchange channels of this invention.

FIG. 12 is a further modification of reactant and heat exchange channels of this invention .

FIG. 13 is perspective view of a modified heat exchange channel for this invention.

DETAILED DESCRIPTION OF THE INVENTION

The apparatus of this invention is useful for many tubular reactor applications. Processes suitable for the use of this apparatus will pass liquid, gaseous, or mixed phase fluids together through a tubular reactor. The fluid components may be reactants, catalysts, diluents or any other process stream. Processes carried out in the conduit of the reactor may operate at high or low temperatures in a wide range of pressure conditions including partial vacuums and critical pressure conditions. The fluids passing through the conduit of the reactor may also include liquids having fine particles dispersed therein. Such solids are usually particulate catalysts. Suitable reactor arrangement will not ordinarily retain a fixed or compact moving bed of particulate catalyst.

An example of a suitable process for the reactor of this invention is oligomerization of ethylene to linear alpha-olefins by a homogeneously catalyzed reaction. The reaction is highly exothermic and a typical process of this type commonly requires contact between two liquid phase streams and one vapor phase stream. It is also necessary to maintain uniformity of mixing for product selectivity purposes.

FIG. 1 shows the apparatus of this invention. As depicted in FIG. 1, the apparatus includes a tubular reactor in the form of an elongated conduit 4 that provides the containment conduit for the tubular reactor. The tubular reactor houses multiple mixing devices 5, 6, and 7. A fluid stream enters the tubular reactor through the bottom of conduit 4 via an inlet 8 and exits the top of the conduit 4 through an outlet 9. Fluid that flows into the conduit 4 from inlet 8 first enters an upstream chamber 16 defined as the volume between inlet 8 and mixing device 5. Reactant fluid flow from chamber 16 next enters a plurality of channels 10 having open bottoms and tops for fluid flow therethrough. The walls of channels 10 are irregular to provide turbulence and mixing of the fluid as it passes up the channels. Heat exchange channels 14 extend between reaction channels. A heat exchange fluid passes through channels 14 to simultaneously heat or cool the reactants in the reaction channels 10. The tops and bottoms of heat exchange channels 14 are closed to fluid flow and independent nozzles or preferably, as hereinafter more fully illustrated, a manifold system distributes and collects the heat exchange fluid at each mixing device location. As fluid continues to pass upwardly out of mixing device 5 it enters an intermediate chamber 17 defined as the space between mixing devices 5 and 6. Intermidiate chamber 17 series as a mixing device provides a zone for recombination of the reactant flow from the reactant channels of mixing device 5. Continued upward flow passes the reactant fluid to mixing device 6 which further mixes the reactant fluid while simultaneously heating or cooling the reactant fluid with a heat exchange fluid.

This invention can use any type of plate to define the reaction channels and the heat exchange channels. By necessity, suitable plates have minimum thickness to promote rapid heat exchange across the plates and to minimize

the amount of cross sectional flow area removed from the conduit reactor by the presence of the plates in the mixing devices. Maintaining channel widths between the plates can be accomplished by using various spacers. The spacers between the plates have the advantage of providing additional surface and edges for introducing any desired shearing forces on the fluid as it passes through the mixing devices. Suitable spacers also can provide a controlled degree of turbulence for the reactants as they pass through the reaction channels. Turbulence from spacers also helps promote heat exchange by introducing turbulence into both the heat exchange fluid and the reactant fluids. Typically, the heat exchange channels and reaction channels will have an average width in a range of from a ¼ to 2 inches.

Suitable plates for this invention will comprise any plates that allow a high heat transfer rate and that are easily secured in the reaction section in a stable configuration that readily retains the channel arrangement. Thin plates are preferred and usually have a thickness of from 1 to 2 mm. The plates are typically composed of ferrous or non-ferrous alloys such as stainless steel. Each plate has some means of introducing turbulence and preferably has corrugations that are inclined to the flow of reactants and heat exchange fluid.

The plates may be formed into curves or other configurations, but flat plates are generally preferred for stacking purposes.

A preferred form of the plate elements consists of corrugated plates. Corrugated plates, when stacked next to each other, have the advantage of defining the channel spacing while simultaneously supporting the adjacent plate elements and providing a complex flow path that introduces turbulence mixing to the fluid. The corrugated plates may be stacked directly next to each other with the space between corrugations defining alternate reactant channels and heat exchange channels. Where plates contain inclined corrugations, the plates may be stacked next to each other to define the heat exchange and reactant flow channels as the area between corrugations. Preferably the corrugation pattern will be reversed between adjacent plates so that a herring bone pattern on the faces of opposing corrugated plates will extend in opposite directions and the opposing plates faces may be placed in contact with each other to form the is flow channels and provide structural support to the plate sections.

In the case of corrugated plates the corrugation pattern may be varied to achieve a variety of contacting and reaction effects. Such effects include increased turbulence for improving the contacting between the components by varying the pitch of the corrugation. The degree of turbulence may also be controlled by varying the amplitude of the corrugations and the frequency of the corrugations,which are otherwise referred to as the pitch and the depth of the corrugations. Corrugations having a large pitch or low frequency and shallow depth or low amplitude will provide a low degree of turbulence. Increasing either or both of the frequency and amplitude will raise the degree the turbulence. Suitable corrugated plates are described in detail in U.S. Pat. No. 5,525,311; the contents of which are hereby incorporated by reference. The average channel width for reactant channels of this invention will typically range of from ¼ to 2 inches when using corrugated plates. The average width of the corrugated plates is most accurately computed by calculating the volume of the channel and dividing it by the transverse cross sectional area of the channel.

Mixing device 6 contains reactant and heat exchange channels essentially identical to those shown in mixing device 5 except for their orientation. The channels 10 and 14 in mixing device 5 extend in a direction perpendicular to the section of FIG. 1. The channels of mixing device 6 extend in the same direction as the section of FIG. 1. The ninety degree change in orientation of the reactant and heat exchange channels between mixing devices 5 and 6 further promotes intermixing of the reactant fluid between mixing stages. Accordingly, FIG. 1 shows the transverse profile of one heat exchange plate 15 in mixing device 6 and the corrugated surface defined thereon which introduces turbulence into the fluid passing through the reactant and the heat exchange channels. The heat exchange fluid is supplied to the heat exchange channels of mixing device 6 via a nozzle 18 and withdrawn from the heat exchange channel via a nozzle 20. After heating or cooling by the heat exchange fluid, mixing device 6 discharges the reactant fluid into a downstream chamber 22.

Downstream chamber 22 is the volume of conduit 4 between mixing device 6 and the outlet 9. Both upstream chamber 16 and downstream chamber 22 may contain additional mixing devices. FIG. 1 illustrates downstream chamber 22 with an additional mixing device 7 with channels oriented 90 degrees from the channels in mixing device 6 and through which the reactant fluid passes on its upstream course to outlet 9. In a highly preferred embodiment, the apparatus of this invention will have at least 3 and as many as 10 or more of the mixing devices. Chambers 16, 17, and 22 can provide means for and may contain additional mixing devices that do not have indirect heat exchange capacity. However, apart from any means for adding or withdrawing fluids, chambers 16, 17, and 22 usually provide means for unobstructed fluid flow between mixing devices in the chambers. Thus, the chambers between mixing devices are normally open for free flow of fluids except for any small intermediate inlet or outlet nozzles (not shown).

Intermediate inlet or outlet nozzles for withdrawing fluids from the conduit 4 at locations intermediate to inlet end 8 and outlet end 9 are normally positioned between the mixing devices. Fluids may be added to supply additional reactants or diluents for reaction control. Fluids may also be withdrawn, heated or cooled, and returned to conduit 4 for purposes of temperature control. The addition or withdrawal of fluids through intermediate nozzles will not ordinarily contribute significantly to mixing or dispersion of the fluids between the mixing devices.

The operation of the mixing devices of this invention is often enhanced by the presence of the gaseous medium which breaks the liquid up into fine droplets. The invention can operate in a large range of relative liquid to gaseous composition. Preferably, the quantity of gaseous material is at least equal to 0.2 wt. % of the combined mixture. In operations of the reactor wherein all of the process streams are in normally in liquid phase, changes to the process may be effected to promote high shear mixing by the addition of gases. The high shear force enhancement of gases may be obtained by injecting an inert gas with the liquids entering the reactor. Injection of the gas with the liquids may be regulated to obtain a controlled level shear force with relatively constant pressure drop.

In this arrangement, sequential mixing of increased severity can be provided by varying the plate arrangement and/or shearing elements in each mixing device along the fluid flow path through the reactor. As a result repeated mixing and varied intensity mixing can be achieved through multiple mixing devices within a single conduit 4.

Regardless of the number of mixing devices contained within conduit 4, the upstream and downstream chamber

will preferably have an open length equal to at least twice the inside diameter of conduit **4**. This open length prevents direct injection or direct withdrawal from any of the mixing devices so that each mixing device fully performs its function.

Nozzles **18** and **20** provide one means for passing a heat transfer fluid through a narrow system of isolated heat exchange channels while maintaining open tops and bottoms of reactant channels for continuous fluid flow therethrough. FIGS. 2 and 3 show a manifolding arrangement that allows insertion of the plurality of narrow heat exchange channels into the conduit of the reactor. Looking then at FIG. **2**, nozzle **18** delivers an inflow of heat exchange fluid to a distribution space **24** having open communication with the heat exchange channels across the sides thereof while being blocked from communication with the reactant channels across the same surface. Similarly, nozzle **20** withdraws heat exchange fluid from a collection space **26** which again has open communication with the heat exchange channels across the sides of plates **15** while the spaces between plates **15** are closed to communication with the reactant channels.

As more fully appreciated from FIG. **3**, the bundle of corrugated plates **15** defining the heat exchange and reactant channels are placed next to each other to build a stack of plates defining the alternate heat exchange and reactant channels. The entire stack of plates **15** may be joined at the top and bottom by a ring **27** that is sealed around its inner edge **28** to the heat exchange channels **29** and the reactant channels **30**. The entire mixing device **6** may be assembled outside of the tube **4** and inserted into the tube at the location of nozzles **18** and **20**. Seal welds **31** at the top and bottom of mixing device **6** prevents any mixing between the heat exchange fluid and the reactant stream.

The separate communication of the heat exchange channels and reactant channels with the heat exchange and reactant fluid respectively can again be more fully appreciated from FIG. 3. The upper portion of split section **3-3** shows the heat exchange channels **29** closed to communication with the upper chamber **22** to isolate the heat exchange fluid from the reactant fluid. Similar closure of the heat exchange channels is provided at the bottom of the mixing device **6**. The reactant channels **30** are open at both the top and the bottom of mixing device **6**. As shown on the right side of FIG. **3**, heat exchange fluid is selectively collected only from heat exchange channels **29** by closing the side of reactant channels **30** across openings **32** at the sides where the reactant channels **30** encounter the collection space **26**. Conversely, the ends **33** where the heat exchange channels end at collection space **26** have openings **33** for open communication therewith. Plates **15** are stacked in a direction transverse to the channels such that the plates press against the inside wall of tube **4**. Pressing the plates against the inside wall of tube **4** prevents bypassing of the heat exchange fluid by at least partially blocking the flow of heat exchange fluid between the transverse side of the stacked plates and the inside of tube **4**. A complete blockage of heat exchange flow at this section is not necessary or desired in order to maintain a good distribution of the heat exchange fluid across all of the heat exchange channels **29**. Distribution channel **24** has a similar arrangement of openings and closures with the heat exchange channels and reactant channels as those shown for collection space **26**.

FIGS. **4** and **5** show a modified mixing device **6'** similar to that shown in FIGS. 1–3. FIGS. **4** and **5** differ by showing an alternate method for circulating the heat exchange fluid through the heat exchange channels. The arrangements shown in FIGS. **4** and **5** collects and withdraws the heat exchange fluid from a single side of a containment tube **4'**. Nozzles **34** and **35** supply heat exchange fluid to heat exchange channels **36** and **37**, respectively, through distribution spaces **38** and **39**. Nozzles **40** and **41** collect heat exchange fluid from heat exchange channels **42** and **43**, respectively, through collection spaces **44** and **45**. A series of partitions **46** separate the collection spaces from the distribution spaces. Similar to that described in FIG. **3**, closures **47** prevent fluid from entering the reactant channels **30'** while openings **48** permit free flow of heat exchange fluid to the collection spaces **44** and **45**. A series of radially extending manifolds **50** interconnect the heat exchange channels **36** and **37** that receive the incoming heat exchange fluid with the heat exchange channels **42** and **43** from which the heat exchange fluid is collected. Manifolds **50** have closures **51** where the manifolds register with the sides of the reactant channels **30'** and openings **52** where the manifolds register with the heat exchange channels. Openings **52** function in a manner analogous to that described for openings **38**, **39**, **45**, and **48**. Manifolds **50** are shown as intermittently spaced down the side of mixing device **6'** that lies opposite the distribution and collection spaces. Connecting manifold **50** may have completely open interiors since there is no need to control fluid flow from the different collection or distribution nozzles. Manifold **50** may be either intermittent as shown or cover the entire side of the mixing device **6'** as a continuous manifold. Where manifold **50** is intermittently spaced, the entire side area of the reactants and the heat exchange channels are closed to fluid flow between the manifolds. Mixing device **6'** may be inserted into tube **4'** in a fully assembled state and secured within the tube and registered in sealing communication with the collection and distribution nozzles by providing seal welds **53** at the top and bottom of mixing device **6"**.

FIGS. **6–10** show a further alternate manifolding arrangement for use with a square conduit arrangement that retains the mixing devices in the conduit reactor. In this arrangement reactants again flow axially through the conduit **55** from an inlet **56** to an outlet **57**. Internally, conduit **55** retains mixing devices **58** and **59** between open mixing chambers **60**. Mixing devices **58** and **59** contain a similar arrangement of channels that alternately retain heat exchange fluid or provide passage of the reactants axially through the reactor conduit **55**. Again, mixing devices **58** and **59** alternate the orientation of the reactant channels by **90** degrees relative to each other. Fluid is supplied to mixing device **59**, and any similarly oriented mixing devices (not shown), by a nozzle **61** via a distribution space **63** while a distribution space **64** withdraws heat exchange fluid from mixing device **59** for removal via nozzle **62**. A nozzle **66** (See FIGS. **7–9**) provides heat exchange fluid to mixing device **58** and a nozzle **65** withdraws a heat exchange fluid that has passed through mixing device **58**. Distribution and collection manifold spaces, similar to those shown for mixing device **59**, communicate mixing device **58** with nozzles **66** and **65**.

As can be more fully appreciated from FIGS. **7–9**, the reactor-conduit arrangement of FIGS. **6–10** accommodates a

square or rectangular reactor design. The square design facilitates fabrication and assembly of the necessary plate elements. As more fully seen from FIG. 7–10, a curved channel **67** may provide the manifold space **63**. The sides of the reaction channels that meet with the manifold spaces **63** are again closed to communication with the heat exchange fluid. Sealing the ends of curved channel **67** at the corners of mixing devices **59** furnishes an efficient shape for withstanding internal pressure while also providing a convenient method for distribution of fluids. Having channels extending on all four sides of the mixing conduit arrangement **55** conveniently affords a pressure balancing function for the relatively thin plates that define the heat exchange channels. Specifically, when looking at FIG. 7, the curved channel **68** balances the pressure on outermost plates of mixing devices **59** to minimize any pressure loading across the flat surface of the plate and thereby prevents deformation without requiring a thick plate gauge. Looking at FIG. 8, the curved channels **67** and **68** also contribute support to the walls **70** of the open chamber sections **60** that have a flat profile and poor pressure loading capability.

FIG. 9 shows a modified form of the invention where an outer circular conduit or pipe furnishes the curved chamber portions. The inside diameter of the pipe **74** slightly exceeds the diagonal dimension across the mixing device **59**. The cross section as represented in FIG. 9 can simplify the construction of the conduit reactor arrangement. The outer wall may comprise a simple pipe cut in half across the section line **71**. Assembly may consist of inserting the reaction stack into the one half of pipe **74** and seal welding the mixing device therein at points **73**. Longitudinally welding the other half of the pipe **74** back to the other pipe half at points **73** completes pressure containment of the reaction stack. This procedure assembles a reactor mixer with pressure balancing, distribution manifolds and collection manifolds in a highly efficient pressure resisting shape with a few simple operations. No criticality attaches to the seal between mixing devices at corners **75** since communication between adjacent distribution manifolds **76** and between adjacent collection manifolds **77** will not adversely effect the circulation of the heat transfer fluid.

As illustrated by FIG. **10**, the mixing devices may have rectilinear shapes other than a square. Suitable curved channels **78** may accommodate any length of reactant and heat exchange channels to provide rectangles with varied aspect ratios. Smaller curved channels **79** sized to suit the minor transverse dimension of the reaction conduit may still serve a useful pressure balancing function.

The heat exchange channels and reaction channels need not have a relatively uniform or equal width. The relatively narrow dimension of most conduit reactors will typically demand less fluid volume in the heat exchange channels than in the reaction channels. Minimizing the volume in the heat exchange channels also lowers the amount of reactant flow blockage imposed by each mixing device. Unlike the channels shown in FIGS. **3** and **5**, FIGS. **11** and **12** represent alternate arrangements for the stacking of the plates to define different widths for the heat exchange and reaction channels.

FIG. **11** depicts an arrangement for the preferred corrugated plates of this invention. As shown by FIG. **11** corrugations need not be defined so that all peaks touch. FIG. **11** shows an arrangement where an offset arrangement of corrugated plate pairs **80**, **81**, and **82** define smaller widths for the heat exchange channels **83** relative to reactant channels **85**. The arrangement of FIG. **11** minimizes the overall reactant flow area blocked by the heat exchange channels in the mixing device.

Alternately, as shown in FIG. **12**, perforated or slotted plates **86** may be inserted between pairs **87** of solid plates to increase the proportion of reactant flow area in the mixing device. Perforated plate **86** permits open communication between reaction channels **88** and provides a greater effective width of the reactant channels as compared to heat exchange channels **89**. The insertion of the corrugated or slotted plate has the additional advantage of providing fluid shear as the reactants pass through reactant channels **88** and further enhance mixing. A perforated insert plate arrangement is shown in U.S. Pat. No. 5,538, 700; the contents of which are hereby incorporated by reference.

FIGS. **13** displays an additional method for introducing shearing on the reactant fluid as it passes through the reaction channels. FIG. **13** shows an arrangement of reaction channels **90** defined by corrugated plates **91**. A shear inducing plate **92** is sandwiched between corrugated plates **91**. Punched tabs **93** extending transversely outward from plate **92** present sharp edges for additional shearing action on the fluid as it passes through the reaction channels **90**.

What is claimed is:

1. A tubular reactor for the plug flow reaction of one or more reactants in the presence of a gas, liquid, or mixed phase fluids, said apparatus comprising:

(a) a containment conduit having an inlet and an outlet end for passing fluid from the inlet end to the outlet end of the conduit and establishing a flow direction through said conduit;

(b) at least two spaced apart mixing sections comprising a stack of plates defining heat exchange flow channels and reactant flow channels, said stack of plates retaining turbulence inducing structures that extend transversely across the reactant flow channels, said stack of plates defining reactant channel inlets at the upstream end of the mixing section and reactant channel outlets for the reactant channels at the downstream end of the mixing section and said stack of plates being stacked in a direction transverse to one of the heat exchange flow channels and the reactant flow channels such that plates on transverse sides of the stack of plates press against the inside wall of the containment conduit to obstruct circumferential flow of fluid around the conduit and other plates in the stack of plates having ends that are spaced apart from the inside wall of the containment conduit;

(c) a distribution manifold for distributing a heat exchange fluid to the sides of the heat exchange channels defined by an annular volume between the inside wall of the conduit and the ends of the plates that are spaced apart from the inside wall of the containment conduit;

(d) a collection manifold for collecting a heat exchange fluid from the sides of the heat exchange channels defined by an annular volume between the inside wall of the conduit and the ends of the plates that are spaced apart from the inside wall of the containment conduit;

and

(e) annular rings covering the annular volume at the upstream and downstream ends of the mixing sections that are welded to the conduit to hold and seal the mixing sections in place.

2. The reactor of claim 1 wherein corrugations defined by said plates define the turbulence inducing structure.

3. The reactor of claim 1 wherein the plates define essentially planar channels.

4. The reactor of claim 3 wherein the channels in adjacent mixing devices extend in a direction normal to each other.

5. The reactor of claim 1 wherein a first nozzle delivers the heat exchange fluid to one side of the annular volume and a second nozzle withdraws the heat exchange fluid from an opposite side of the annular volume.

6. The reactor of claim 5 wherein the distribution manifold distributes the heat exchange fluid to a first group of said heat exchange channels on a first side of said mixing device, a recirculation manifold communicates said first group of heat exchange channels with a second group of heat exchange channels on an opposite side of said mixing device and the collection manifold collects heat exchange fluid from said second group of heat exchange channels on the first side of said heat exchange device.

7. The reactor of claim 1 wherein a perforated sheet extends between the plates defining the heat exchange channels to cause a shearing action on the reactant fluid as it passes through heat exchange channels.

8. The reactor of claim 1 wherein said plates comprise imperforate corrugated plates and a perforated corrugated plate extends between the imperforate corrugated plates that define each heat exchange channel.

* * * * *

US005080882A

United States Patent [19]

Yoshimoto et al.

[11] **Patent Number: 5,080,882**

[45] **Date of Patent: Jan. 14, 1992**

[54] **METHODS OF OZONE DECOMPOSITION AND CATALYST STRUCTURES USED THEREIN**

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[30] **Foreign Application Priority Data**

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Apr. 7, 1989	[JP]	Japan	1-088996
Apr. 22, 1989	[JP]	Japan	1-102908

[51] **Int. Cl.**[5] **C01B 13/00**

[52] **U.S. Cl.** **423/579**; 423/219

[58] **Field of Search** 423/219, 579; 502/527

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Attorney, Agent, or Firm—Wegner, Cantor, Mueller & Player

[57] **ABSTRACT**

There is disclosed a catalyst structure for ozone decomposition which comprises a thin porous carrier material which has many micropores in the direction of the thickness of the carrier material and has an ozone decomposition catalyst supported thereon.

Also disclosed is a method of ozone decomposition using such a catalyst structure, in which preferably the catalyst structure comprises a thin porous carrier material which has many micropores not less than 30 μm in diameter in the direction of the thickness of the carrier material and has an ozone decomposition catalyst supported thereon. The carrier material may be of an electrically resistant material, and may be electrified and heated while a gas containing ozone is forcibly passed therethrough.

8 Claims, 2 Drawing Sheets

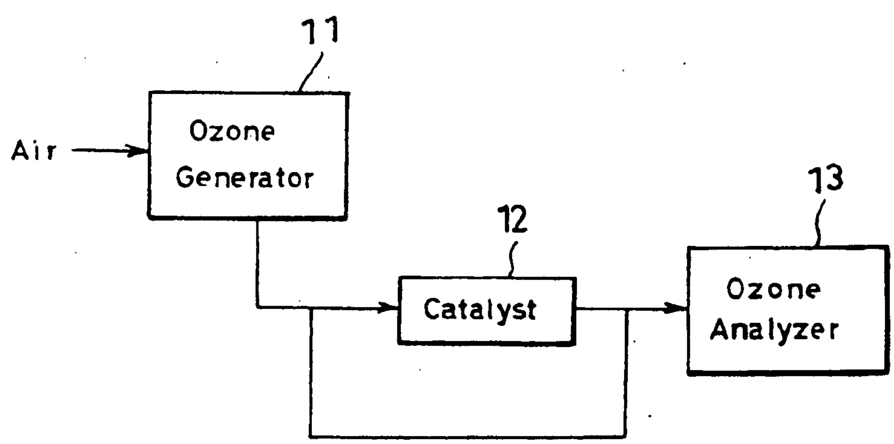


Fig.1

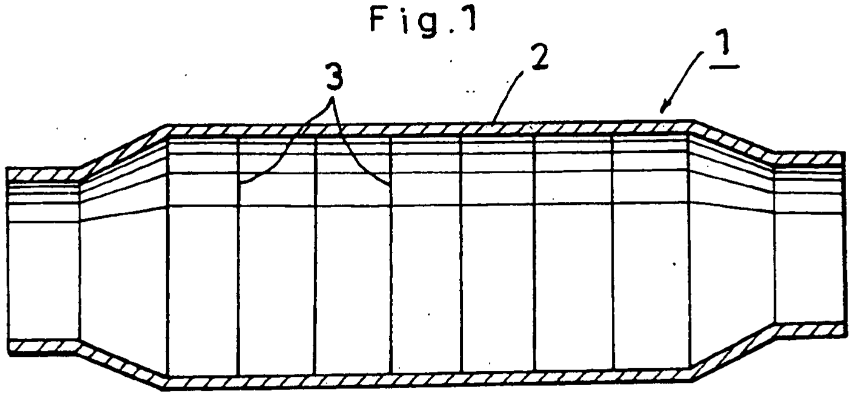


Fig.2

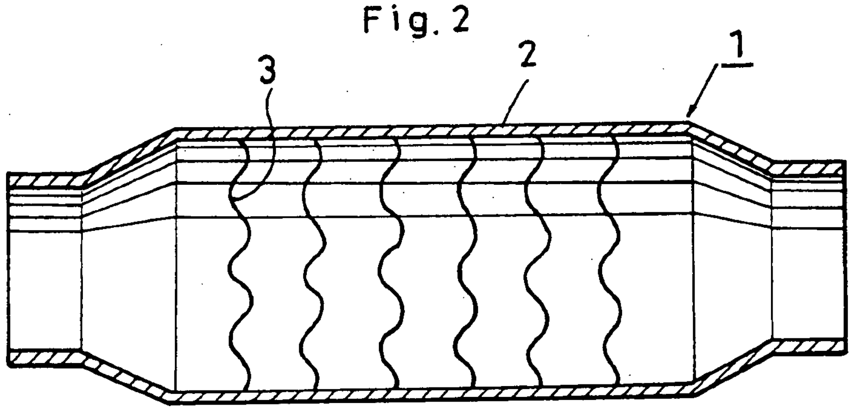


Fig.3

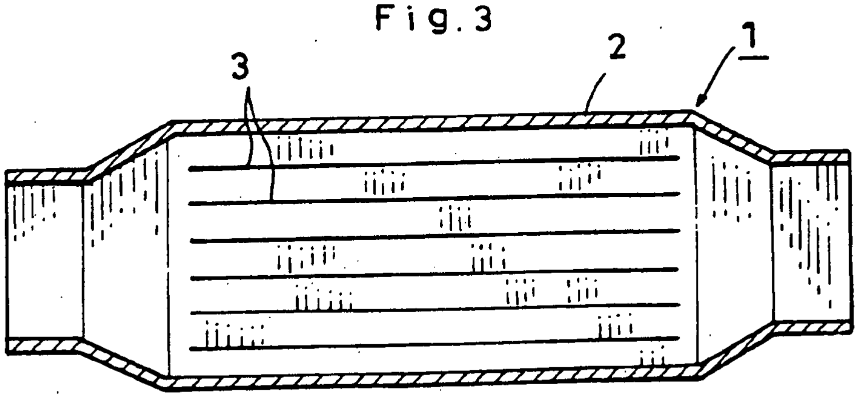


Fig. 4

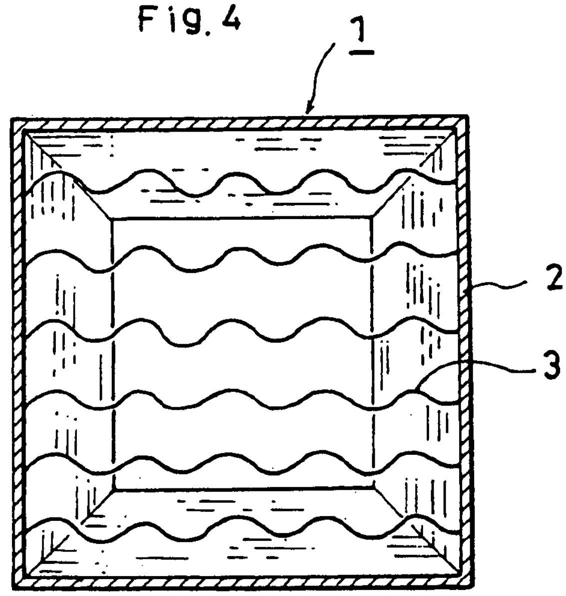
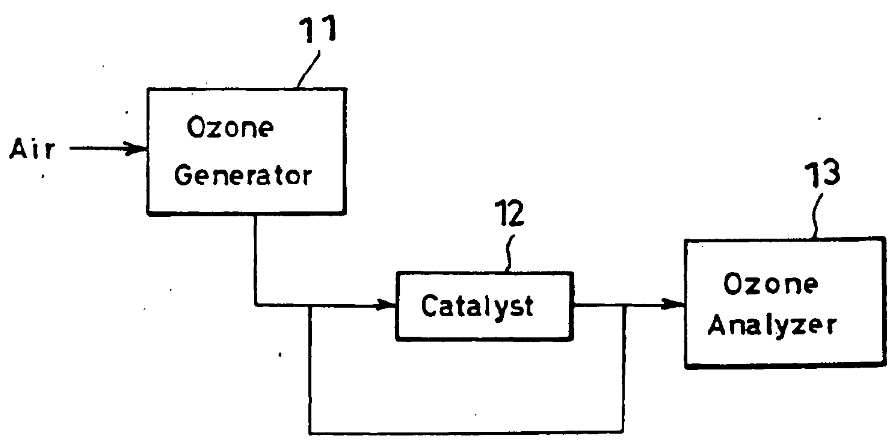


Fig. 5



METHODS OF OZONE DECOMPOSITION AND CATALYST STRUCTURES USED THEREIN

This invention relates to a method of decomposing ozone which is contained, for example, in the air, and a structure, preferably a catalyst structure, having an ozone decomposition catalyst supported thereon, suitably used therein.

There have been proposed various methods of decomposing noxious ozone contained in the air, for example, an adsorption method wherein a porous material is used such as activated carbon or zeolite, or an oxidative decomposition method wherein a catalyst is used such as manganese dioxide.

However, the above mentioned known methods of ozone decomposition are not satisfactory ones. The adsorption method has a disadvantage in that an adsorbent must be very often regenerated since it is limited in adsorption ability. Therefore, the working is laborious and costs a great deal. The oxidative decomposition method has no such disadvantages as above described, but the known catalysts have insufficient decomposition activity for ozone, but also deteriorate in activity very soon when they are used under severe conditions, for example, when a gas which contains high concentrations of ozone is treated or a gas is treated with a high area velocity.

It is, therefore, an object of the invention to provide a structure, preferably a catalyst structure, having an ozone decomposition catalyst supported thereon.

It is a further object of the invention to provide a method of ozone decomposition using such a structure, in which the ozone decomposition rate is maintained high over a long period of time and no substantial decrease in ozone decomposition rate takes place under severe reaction conditions.

In accordance with the invention, there is provided a catalyst structure for ozone decomposition which comprises a thin porous carrier material which has many micropores in the direction of the thickness of the carrier material and has an ozone decomposition catalyst supported thereon.

Further in accordance with the invention, there is provided a method of ozone decomposition which comprises putting a gas containing ozone therein into contact with a catalyst structure comprising a thin porous carrier material which has many micropores in the direction of the thickness of the carrier material and has an ozone decomposition catalyst supported thereon.

Other features and advantages of the invention will be apparent from the following description taken in connection with the accompanying drawings, in which,

FIG. 1 is a sectional view of an embodiment of the ozone decomposition reactor which contains a catalyst structure according to the invention;

FIGS. 2 and 3 are also sectional views of further embodiments of the ozone decomposition reactor which contains a catalyst structure of the invention;

FIG. 4 is a section of the reactor shown in FIG. 3 in the radial direction of the casing; and

FIG. 5 is a diagram for measurement of ozone decomposition activity of the catalyst.

The thin porous carrier material used in the invention is composed preferably of a metal such as iron, cobalt, molybdenum, titanium, zirconium, chromium, silver, gold, copper, nickel or tin, or an alloy including stainless steels, copper alloys, nickel alloys, tin alloys, chromium alloys, or a ceramic material such as glass, alumina or silicon carbide. Among these are preferred stainless steels such as SUS 430 or 304 from the standpoint of workability, resistivity and resistance to ozone.

The thin porous carrier material used is preferably a net or screen or plate which has a number of micropores of very short length extending in the direction of the thickness of the carrier material. A porous metal plate which has such micropores may be produced by etching a plate or punching micropores in a plate. When the catalyst structure is used in such a manner that a gas containing ozone therein is passed forcibly therethrough, it is preferred that the micropores are not less than 30 μm in diameter to prevent the occurrence of substantial pressure loss in the reaction.

The carrier material has an ozone decomposition catatalyst supported thereon. Any known catalyst is usable, which includes a metal oxide such as MnO_2, Fe_2O_3, Ag_2O, NiO or CuO, a noble metal such as Pt or Pd, or a mixture of two or more of these. There may be further mentioned, as an effective catalyst, for instance, a Mn containing multicomponent catalyst such as MnO_2-TiO_2, MnO_2-alkali metal or alkaline earth metal oxides; a zeolite containing Cr, Zn, V, W, Fe, Mo, Ni, Co, Ru, Cu, Rh, Pd, Ag or Pt, or an oxide of these metals, a mixture of these; or a zeolite in which K or Na is partly or wholly substituted with such a metal.

The supporting of catalysts on the carrier material will be described hereinafter.

Usually a plurality of the catalyst structures are disposed at intervals in a cylindrical casing to form a catalyst reactor, and a gas containing ozone therein is passed through the reactor to put the gas into contact with the catalyst structure, thereby to catalytically decompose the ozone. The gas may be passed parallel to the catalyst structure in the reactor, or may be forcibly passed through the catalyst structure.

Preferred embodiments of the catalyst reactor will now be described referring to the drawings. FIG. 1 illustrates a reactor 1 embodying the invention which is composed of a cylindrical casing 2 having openings at the ends and a plurality of catalyst structures 3 extending to radial directions of the casing and disposed parallel to each other at intervals in the casing. In FIG. 2 there is illustrated a reactor 1 which contains a catalyst structure 3 composed of porous corrugated nets, plates or sheets. A gas containing ozone therein is introduced from one end of the casing thereinto, and forcibly passed through the catalyst structure, to decompose the ozone. A so-called cleaned gas is discharged from the other end of the casing.

FIG. 3 also illustrates a further embodiment of the reactor 1 which is composed of a cylindrical casing 2 and a plurality of catalyst structures 3 extending to axial directions of the casing and disposed parallel to each other at intervals in the casing. A gas containing ozone therein is introduced into the casing, and the gas is passed parallel to the catalyst structure.

FIG. 4 is a sectional view of the reactor shown in FIG. 3 in the radial direction wherein corrugated sheets or plates are used as a catalyst structure.

In accordance with the invention, a further method of ozone decomposition is provided, which comprises: putting a gas containing ozone therein into contact with an electrically resistant material while electrifying and heating the electrically resistant material.

This method is applicable to the aforedescribed catalyst structure when the carrier material is of an electri-

cally resistant material. It is preferred that the electrically resistant material has such an ozone decomposition catalyst as described hereinbefore supported thereon.

The electrically resistant material used in the invention is composed preferably of a metal such as iron, cobalt, molybdenum, titanium, zirconium, chromium, silver, gold, copper, nickel or tin, or an alloy including stainless steels, copper alloys, nickel alloys, tin alloys, chromium alloys, or a ceramic material such as silicon carbide. Among these are preferred stainless steels such as SUS 430 or 304 from the standpoint of workability, resistivity and resistance to ozone.

The electrically resistant material used is not specifically limited in form, and may be in the form of wire, plate, stick, tube or honeycomb. However, it is preferred that the electrically resistant material is a net or screen or porous plate which has been described hereinbefore. An electrode such as of copper is mounted on the electrically resistant material so that it is electrified and heated when used in the ozone decomposition reaction.

If necessary, the electrically resistant material, preferably a net or plate having an ozone decomposition catalyst supported thereon, may be further worked or combined together, to have a variety of forms or structures.

In the method of the invention, a gas containing ozone therein is put into contact with the electrically resistant carrier material, preferably in the form of net or screen or plate, having an ozone decomposition catalyst supported thereon, while the electrically resistant carrier material is electrified and heated. As before set forth, when the electrically resistant material is used in such a manner that a gas containing ozone therein is passed therethrough, it is preferred that the micropores are not less than 30 μm in diameter.

The catalyst may be supported on a carrier material or an electrically resistant carrier material in any manner. For instance, when a steel wire net or a screen is used as a carrier material or an electrically resistant material, the net is heated in the air to form a layer of oxides on the surface of the wire, and an ozone decomposition catalyst is supported thereon. Alumina may be thermally sprayed on a wire net, and an ozone decomposition catalyst may be supported thereon. Wires of a net may be made porous by solving out in part at the surface layer, and alumina is supported thereon, and then a catalyst may be supported on the alumina.

When an aluminum coated carrier material or an electrically resistant material is used, the aluminum is first oxidized, and thereupon an ozone decomposition catalyst may be supported. Alumina may be supported on a net by an electrophoretic method and thereupon a catalyst may be supported. When a carrier material or an electrically resistant material is of silicon carbide, it may be immersed in an aqueous slurry of a catalyst material, and dried, to support the catalyst thereon directly.

However, the supporting of a catalyst on a carrier material or an electrically resistant material should be interpreted in a broad sense in the invention. Therefore, the following treatments are taken in the invention as embodiments of supporting a catalyst on a carrier material or an electrically resistant material. Namely, it is an embodiment of supporting ferric oxide on a stainless steel wire net to heat the net in the air to produce ferric oxide on the surface of the wire. Further, it is also an embodiment of supporting platinum or palladium on a stainless steel wire net to substitute iron in part with platinum or palladium, which has ozone decomposition activity, by an electrochemical manner.

In accordance with the invention, the electrically resistant net or plate is electrified and heated when a gas containing ozone therein is put into contact therewith. Preferably, the gas is forcibly passed through the net or plate, to decompose the ozone preferably at elevated temperatures effectively, as hereinbefore described.

The temperature of the electrically resistant material in the reaction is not less than 20° C., more preferably not less than 40° C., and most preferably not less than 50° C. When the reaction temperature is less than 20° C., high valency oxides produced when ozone is put into contact with the catalyst are not decomposed, but accumulate in the catalyst, thereby to decrease the activity of the catalyst and ozone decomposition rate in the reaction. On the other hand, when an electrically resistant material having no catalyst supported thereon is used, the material is heated preferably to temperatures of not less than 60° C., more preferably to not less than 100° C.

An allowed maximum temperature at which substantially no decrease in ozone decomposition rate in the reaction occurs is determined by a catalyst used and an amount of ozone per unit amount of the catalyst (molecular weight of ozone per unit time). In the invention there is used as an index to determine the allowed maximum temperature, the product of area velocity and concentration (ppm) of ozone at an inlet of a reactor, the product being referred to as CA value hereinafter. The area velocity is defined as a volume of a reactant gas per unit time (m^3/hr) divided by a gas contact area per volume of catalyst (m^3/m^2).

For instance, when manganese dioxide is used as a catalyst and a CA value of 100,000 is employed, the allowed maximum temperature is 60° C., and when a binary catalyst of MnO_2/Ag_2O and a ternary catalyst of $MnO_2/Ag_2O/TiO_2$ are used, the allowed maximum temperatures are 55° C. and 40° C., respectively. When a CA value of 1000 is employed, the allowed maximum temperatures are 55° C., 50° C. and 35° C., respectively, with the above mentioned unitary, binary and ternary catalysts.

The ozone decomposition rate is dependent upon an area velocity under fixed reaction temperatures and ozone concentrations, but it varies also depending upon a porous material used and its porosity, e.g., meshes when a net is used, and manners in which the material is deposited in a reactor. More specific description will be given in examples.

The structure and method for ozone decomposition of the invention decomposes ozone efficiently over a long period of time with substantially no decrease in ozone decomposition rate.

The invention will now be described more specifically with reference to examples, but the invention is not limited thereto.

EXAMPLE I

Ozone Decomposition with Catalyst Reactors Provided With Porous Carriers Having Catalysts Supported Thereon

A. Preparation of Catalyst Structures

EXAMPLE 1

SUS screens of 50 meshes (wire diameter of 200 μm, wire distance of 300 μm) were cut to a size of 30 mm×30 mm.

An amount of 500 g of manganese dioxide having a specific surface area of 32 m^2/g and micropores of 50 μm average pore size and 100 g of silica sol (Snowtex N by Nissan Kagaku Kogyo K.K.) were fully mixed to provide a slurry of a concentration of 100 g/l.

The screens were immersed in the slurry, air dried at 50° C. and heated at 100° C. for eight hours, to provide catalyst structures having MnO_2 supported thereon.

Seven of the screens thus treated were deposited parallel in a cylindrical casing to extend in the radial direction of the casing with a distance of 70 mm between the first and the last screen to form a catalyst reactor. The reactor had a gas contact area of 100 m^2/m^3 per unit volume.

EXAMPLE 2

An amount of 500 g of manganese dioxide/silver oxide (80/20 in a weight ratio) coprecipitate having a specific surface area of 59 m^2/g and micropores of 30 μm in average pore size and 100 g of silica sol (Snowtex N by Nissan Kagaku Kogyo K.K.) were fully mixed to provide a slurry of a concentration of 100 g/l.

The same screens as in the Example 1 were treated with the slurry in the same manner as in the Example 1, to provide catalyst structures having a binary catalyst of MnO_2/Ag_2O supported thereon.

The screens thus treated were deposited in the same manner as in the Example 1, to form a reactor.

EXAMPLE 3

An amount of 500 g of manganese dioxide/titanium dioxide/silver oxide (70/20/10 in a weight ratio) coprecipitate having a specific surface area of 52 m^2/g and micropores of 30 μm in average pore size and 100 g of silica sol (Snowtex N by Nissan Kagaku Kogyo K.K.) were fully mixed to provide a slurry of a concentration of 100 g/l.

The same screens as in the Example 1 were treated with the slurry in the same manner as in the Example 1, to provide catalyst structures having a ternary catalyst of $MnO_2/TiO_2/Ag_2O$ supported thereon.

The screens thus treated were deposited in the same manner as in the Example 1, to form a reactor.

EXAMPLE 4

SUS thin plates of 100 μm thickness which had aluminum plated thereon in about 10 μm thickness was formed into corrugated plates. The plate was heated in air at 900° C. for one hour, to produce alumina on the surface.

The plates were then treated in the same manner as in the Example 3 to provide catalyst structures having a ternary catalyst of $MnO_2/TiO_2/Ag_2O$ supported thereon.

The plates were deposited parallel in a casing to extend in the axial direction of the casing as illustrated in FIGS. 3 and 4, to form a reactor. The corrugated plates

had a height of 2.5 mm and a pitch of 4.0 mm, and a length of 70 mm in the axial direction of the casing and a width of 30 mm. Thus, the reactor had a gas contact area of about 1200 m^2/m^3 per unit volume.

COMPARATIVE EXAMPLE 1

A honeycomb structure of ceramic fiber corrugated sheets having a gas contact area of about 1200 m^2/m^3 per unit volume (Honeycle by Nichiasu K.K.) was immersed in the same slurry as in the Example 4, air dried at 50° C., and heated at 100° C. for eight hours, to provide a catalyst structure.

The catalyst structure was placed in a Pyrex tube with ceramic fibers as a sealant, to provide a reactor.

B. Measurement of Ozone Decomposition Rate

Ozone decomposition rate was measured with the catalyst reactors manufactured in the Examples 1–4 and Comparative Example 1 as illustrated in FIG. 5, in which, air was introduced into an ozone generator **11** to generate air containing ozone in an appropriate concentration. The air was then sent to the catalyst reactor **12** to catalytically decompose the ozone in the reactor. The ozone concentration in the air was determined with an ozone analyzer **13** at the inlet and the outlet of the reactor. Ozone decomposition rate (%) is calculated based on the expression:

$$\frac{\text{Ozone Concentration at Inlet} - \text{Ozone Concentration at Outlet}}{\text{Ozone Concentration at Inlet}} \times 100\ (\%).$$

The reaction was carried out at a temperature of 20° C. with an ozone concentration at the inlet of the reactor of 0.2 ppm and an area velocity of 10 m^3/m^2. The results are shown in the Table 1.

TABLE 1

	Ozone Decomposition Rates (%)
Example 1	88.5
Example 2	90.7
Example 3	91.8
Example 4	87.1
Comparative 1	75.3

EXAMPLE II

Ozone Decomposition with Catalyst Reactors Provided With Porous Materials Having Catalysts or No Catalysts Supported Thereon While Electrifying the Material

Example 1

SUS screens of 50 meshes (wire diameter of 200 μm, wire distance of 300 μm) were cut to a size of 30 mm×35 mm, and electrodes were mounted on the longer sides.

Seven of these screens thus prepared were deposited parallel in a cylindrical casing to extend in the radial direction of the casing with a distance of 70 mm between the first and the last screen to form a catalyst reactor. The reactor has a gas contact area of 100 m^2/m^3 per unit volume.

Example 2

An amount of 500 g of manganese dioxide having a specific surface area of 59 m^2/g and micropores of 30

μm in average pore size and 100 g of silica sol (Snowtex N by Nissan Kagaku Kogyo K. K.) were fully mixed to provide a slurry of a concentration of 100 g/l.

The same screens as in the Example 1 were treated with the slurry in the same manner as in the Example 1, to provide catalyst structures having a catalyst of manganese dioxide supported thereon.

The screens thus treated were deposited in the same manner as in the Example 1, to form a reactor.

Example 3

An amount of 500 g of MnO_2Ag_2O (80/20 in a weight ratio) coprecipitate having a specific surface area of 59 m^2/g and micropores of 30 μm in average pore size and 100 g of silica sol (Snowtex N by Nissan Kagaku Kogyo K. K.) were fully mixed to provide a slurry of a concentration of 100 g/l.

The same screens as in the Example 1 were treated with the slurry in the same manner as in the Example 1, to provide catalyst structures having a binary catalyst of MnO_2/Ag_2O supported thereon.

The screens thus treated were deposited in the same manner as in the Example 1, to form a reactor.

EXAMPLE 4

An amount of 500 g of $MnO_2/TiO_2/Ag_2O$ (70/20/10 in a weight ratio) coprecipitate having a specific surface area of 52 m^2/g and micropores of 30 μm in average pore size and 100 g of silica sol (Snowtex N by Nissan Kagaku Kogyo K. K.) were fully mixed to provide a slurry of a concentration of 100 g/l.

The same screens as in the Example 1 were treated with the slurry in the same manner as in the Example 1, to provide cayalyst structures having a ternary catalyst of $MnO_2/TiO_2/Ag_2O$ supported thereon.

The screens thus treated were deposited in the same manner as in the Example 1, to form a reactor.

Example 5

SUS thin plates of 100 μm a thickness which had aluminum plated thereon in about 10 μm thickness were formed into corrugated plates. The plates were heated in air at 900° C. for one hour, to produce alumina on the surface.

The plates were then treated in the same manner as in the Example 4 to provide catalyst structures having a ternary catalyst of $MnO_2/TiO_2/Ag_2O$ supported thereon.

The corrugated plates were deposited in a casing as illustrated in FIGS. 3 and 4, to form a reactor. The corrugated plates had a height of 2.5 mm and a pitch of 4.0 mm, and a length of 70 mm in the axial direction of the casing and a width of 30 mm. Thus, the reactor had a gas contact area of about 1200 m^2/m^3 per unit volume.

B. Measurement of Ozone Decomposition Rate

Ozone decomposition rate was measured with the catalyst reactors manufactured in the Examples 1-5 in the same manner as in the Example I, at a temperature of 20°-70° C. (by electrifying to heat electrically resistant carrier material when needed) with varied ozone concentrations at the inlet of the reactor and area velocities so that CA values were in the range of 100-10,000. The ozone decomposition rate was measured at the initial stage, after 100 hours and 1000 hours, respectively. The results are shown in the Table 2.

TABLE 2

	Temperature of Carrier Material (°C.)	Ozone Concentration at Inlet (ppm)	CA Values*)
Example 1	50	100	1000
	60	100	1000
	70	100	1000
Example 2	20	1000	1000
		500	5000
		1000	10000
	30	100	1000
		500	5000
		1000	10000
	50	100	1000
		500	5000
		1000	10000
Example 3	30	1000	10000
	40	1000	10000
	50	1000	10000
Example 4	30	1000	10000
	40	1000	10000
	50	1000	10000
Example 5	30	1000	10000
	40	1000	10000
	50	1000	10000

	Ozone Decomposition Rate		
		After	
	Initial	100 hours (%)	1000 hours
Example 1	87.3	12.4	5.1
	92.5	64.1	27.7
	96.3	95.4	95.1
Example 2	84.8	49.7	10.3
	81.3	37.4	9.1
	78.4	31.0	8.5
	90.4	62.9	22.2
	86.9	50.8	14.5
	80.1	35.0	8.8
	96.9	96.5	96.7
	92.0	87.5	67.5
	88.1	80.7	48.3
Example 3	98.6	95.3	47.2
	99.9	99.5	90.3
	100	100	97.2
Example 4	98.3	94.9	77.6
	99.6	98.4	94.9
	100	100	100
Example 5	98.3	94.9	74.0
	99.6	98.4	96.1
	100	100	100

*)ppm · m^3/m^2 · hr

EXAMPLE II

Ozone Decomposition with Catalyst Reactors Provided With Porous Materials Having Catalysts or No Catalysts Supported Thereon While Electrifying the Material

Example 1

SUS thin plates of 500 μm thick were cut to a size of 70 mm×35 mm, and electrodes were mounted on the longer sides.

Six of these plates were deposited parallel in a cylindrical casing to extend in the axial direction of the casing with a distance of 5 mm therebetween, as illustrated in FIG. 3, to form a reactor. The reactor had a gas contact area of 100 m^2/m^3 per unit volume.

EXAMPLE 2

An amount of 500 g of manganese dioxide having a specific surface area of 32 m^2/g and micropores of 50 μm in average pore size and 100 g of silicasol (Snowtex

N by Nissan Kagaku Kogyo K. K.) were fully mixed to provide a slurry of a concentration of 100 g/l.

The same plates as in the Example 1 were heated in air at 500° C. for one hour, and then were immersed in the slurry, air dried at 50° C. and heated at 100° C. for eight hours, to provide catalyst structures having manganese dioxide supported thereon.

The catalyst structures were then deposited in the same manner as in the Example 1, to form a reactor.

EXAMPLE 3

An amount of 500 g of MnO_2/Ag_2O (80/20 in a weight ratio) coprecipitate having a specific surface area of 59 m^2/g and micropores of 30 μm in average pore size and 100 g of silica sol (Snowtex N by Nissan Kagaku Kogyo K.K.) were fully mixed to provide a slurry of a concentration of 100 g/l.

The same plates as in the Example 1 were heated in air at 500° C. for one hour, and then were immersed in the slurry, air dried at 50° C. and heated at 100° C. for eight hours, to provide catalyst structures having a binary catalyst of MnO_2/Ag_2O supported thereon.

The catalyst structures were then deposited in the same manner as in the Example 1, to form a reactor.

EXAMPLE 4

An amount of 500 g of $MnO_2/TiO_2/Ag_2O$ (70/20/10 in a weight ratio) coprecipitate having a specific surface area of 52 m^2/g and micropores of 30 μm in average pore size and 100 g of silica sol (Snowtex N by Nissan Kagaku Kogyo K. K.) were fully mixed to provide a slurry of a concentration of 100 g/l.

The same plates as in the Example 1 were heated in air at 500° C. for one hour, and then were immersed in the slurry, air dried at 50° C. and heated at 100° C. for eight hours, to provide catalyst structures having a ternary catalyst of $MnO_2/TiO_2/Ag_2O$ supported thereon.

The catalyst structures were then deposited in the same manner as in the Example 1, to form a reactor.

Example 5

SUS wires of 2 mm in diameter which had aluminum thermally sprayed thereon in about 10 μm thickness were heated in air at 900° C. for one hour, to produce alumina on the surface.

The wires were treated in the same manner as in the Example 4 to provide catalyst structures having a ternary catalyst of $MnO_2/TiO_2/Ag_2O$ supported thereon.

The wires were arranged parallel in a casing to extend in the axial direction of the casing at intervals of 5 mm, as illustrated in FIG. 3, to form a reactor. The effective length in total of the wires was 175 mm, so that the reactor had a gas contact area of about 17.5 m^2/m^3 per unit volume.

B. Measurement of Ozone Decomposition Rate

Ozone decomposition rate was measured with the reactors manufactured in the Examples 1-5 in the same manner as in the Example II at a temperature of 20°-70° C. The results are shown in the Table 3.

TABLE 3

	Temperature of Carrier Material (°C.)	Ozone Concentration at Inlet (ppm)	CA Values*)
Example 1	50	100	1000
	60	100	1000
	70	100	1000
Example 2	20	1000	1000
		500	5000
		1000	10000
	30	100	1000
		500	5000
		1000	10000
	50	100	1000
		500	5000
		1000	10000
Example 3	30	1000	10000
	40	1000	10000
	50	1000	10000
Example 4	30	1000	10000
	40	1000	10000
	50	1000	10000
Example 5	30	1000	10000
	40	1000	10000
	50	1000	10000

	Ozone Decomposition Rate		
		After	
	Initial	100 hours (%)	1000 hours
Example 1	47.5	6.4	2.6
	72.6	40.1	15.0
	80.8	78.6	78.8
Example 2	61.0	29.1	5.4
	56.8	21.3	4.8
	53.5	24.3	6.8
	69.0	39.1	11.8
	63.8	29.9	7.5
	55.3	19.4	4.5
	82.4	82.8	82.2
	71.7	64.6	43.0
	65.5	56.1	28.1
Example 3	88.4	78.3	27.3
	96.8	92.9	68.9
	98.2	98.2	98.4
Example 4	87.0	76.8	52.7
	93.6	87.4	77.4
	99.5	99.4	99.5
Example 5	47.0	37.4	9.0
	53.7	47.3	40.3
	55.2	55.0	55.0

*) ppm · m^3/m^2 · hr

What is claimed is:

1. A method of decomposing ozone, comprising contacting a gas containing ozone with a porous carrier sheet having an ozone decomposition catalyst supported thereon, said porous carrier sheet composed of an electrically-resistant material having a plurality of micropores not less than 30 μm in diameter in the direction of thickness of the sheet, while electrifying and heating the electrically-resistant material.

2. A method as recited in claim 1, wherein the gas containing ozone is passed through the porous carrier sheet.

3. A method as recited in claim 1, wherein the gas containing ozone is passed along the porous carrier sheet.

4. A method as recited in claim 1, wherein the electrically-resistant material is in the form of a screen.

5. A method as recited in claim 1, wherein the electrically-resistant material is in the form of a corrugated screen, mesh or plate.

6. A method as recited in claim 1, wherein the electrically-resistant material is metal or ceramic.

7. A method as recited in claim 6, wherein the metal is stainless steel.

8. A method as recited in claim 1, wherein the electrically-resistant material is heated to a temperature up to 70° C.

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